



# Urchin-like hollow-structured cobalt oxides with excellent anode performance for lithium-ion batteries



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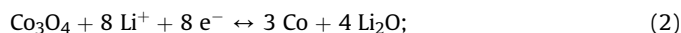
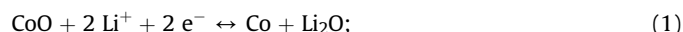
## ABSTRACT

Urchin-like CoO and Co<sub>3</sub>O<sub>4</sub> hollow structures with potential use as anodes in lithium ion batteries were synthesized via the facile thermal decomposition of precipitated amorphous cobalt carbonate hydroxide under either Ar or air. The morphology and, consequently, electrochemical properties of the samples were highly dependent on the precipitation temperature. The cobalt oxides, as derived from precursors that were obtained at room temperature, exhibited superior activity to those obtained at 50 °C and 80 °C because of their unique nanosized architecture. Meanwhile, CoO samples demonstrated much better cyclability and rate capability than Co<sub>3</sub>O<sub>4</sub> samples, as they exhibited much higher coulombic efficiency and lower hysteresis for lithium insertion/extraction. The curved, short, and closely entangled nanowires of CoO sample, which was derived from room temperature precursor, yielded excellent electrochemical performance. The sample displayed a high reversible capacity of about 850 mAh g<sup>-1</sup> at a current density of 500 mA g<sup>-1</sup>, a good stability through 50 cycles with a high coulombic efficiency of about 98%, and a high rate capability of 610 mAh g<sup>-1</sup> even at a rate of 3000 mA g<sup>-1</sup>.

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## 1. Introduction

Current research on negative electrodes for Li-ion batteries (LIBs) is mainly focused on both enhancing the electrochemical performance of commonly used carbonaceous materials through physical and chemical manipulation and finding alternative materials for this application. The first route has been limited by the theoretical capacity of carbonaceous anodes. However, the second approach has led to the discovery of new attractive materials, including Ti-based oxides such as TiO<sub>2</sub> and Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> [1–6], metals or alloys consisted of elements like Sn and Si [7–10], and conversion reaction anode materials such as oxides [11–19], nitrides [20–22], and hydrides [23,24]. Cobalt oxides particularly have been widely studied given their high theoretical capacities. CoO and Co<sub>3</sub>O<sub>4</sub> are the most promising candidates in this class, which theoretically undergo the following reversible reactions:



However, the low capacity retention and poor rate capability underlying the conversion reactions with huge volume changes have restricted their practical application [25,26]. One of the most successful strategies for resolving these problems has been through the fabrication of nanosized structures. A great deal of research have focused on developing materials exhibiting novel morphologies, including nanowires [27,28], nanorods [29], nanoparticles [30], nanosheets [31], and hollow structures [13,26,32]. Generally speaking, hollow microstructures with nanosized subunits and designed voids [13,26,33,34], exhibit especially good electrochemical properties due to the increased mass-electrolyte contact area, shortened Li<sup>+</sup> diffusion distance, and alleviated structural strain that results from repeated lithium insertion-extraction process. Despite significant advancements, it continues to be a challenging issue to improve the rate capacity and cycling stability of cobalt oxide materials.

In this work, we report the simple preparation of urchin-like CoO and Co<sub>3</sub>O<sub>4</sub> hollow structure. Cobalt oxides were synthesized via the thermal decomposition of precipitated amorphous cobalt carbonate hydroxide under Ar or air atmospheres. Unlike previous reports, which have synthesized precursors such as Co(OH)<sub>2</sub>, CoCO<sub>3</sub>, and cobalt carbonate hydroxide under sealed high-pressure conditions

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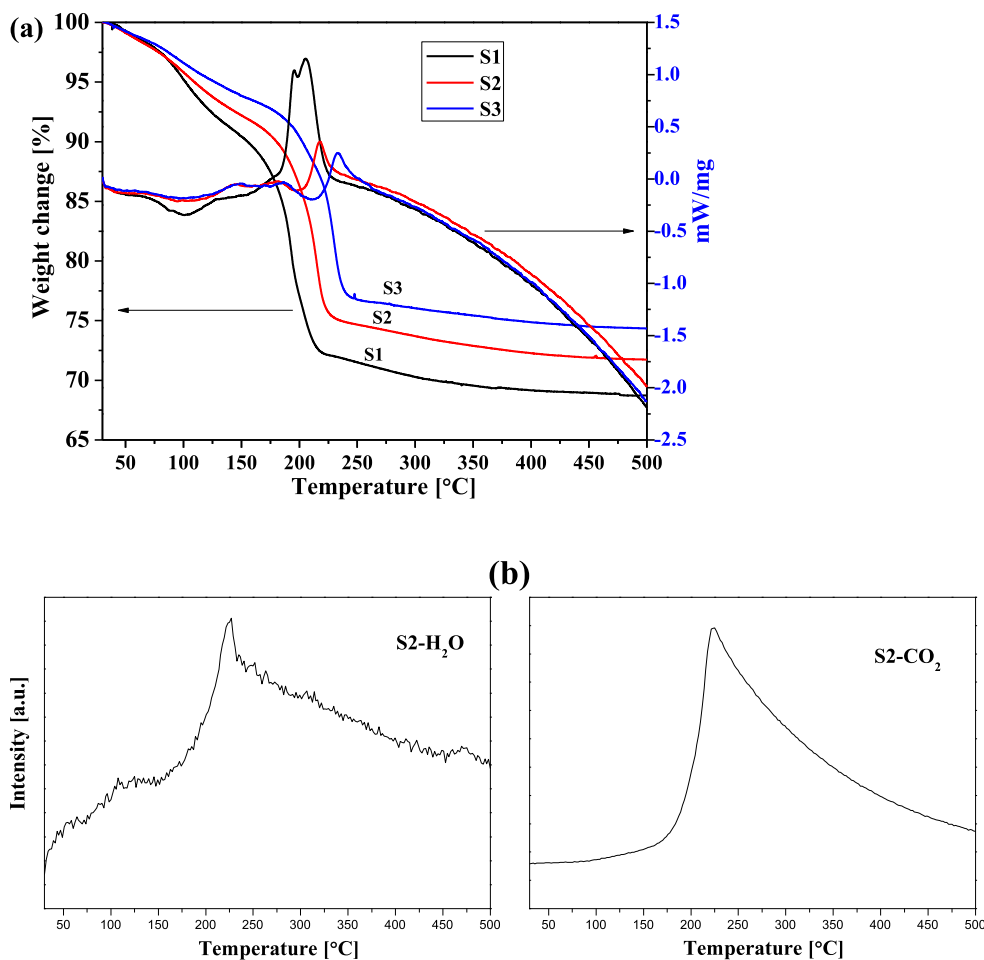


Fig. 1. (a) TG and DSC curves for precursor decomposition under air; (b) MS spectra of water and CO<sub>2</sub> produced as a result of sample decomposition.

and temperatures ranging from 90 to 180 °C [15,31,35–37]. Our procedure employs a scalable precipitation method at/near room temperature. The synthesized cobalt oxide materials show high reversible capacity and superior rate performance.

## 2. Experimental

### 2.1. Preparation of cobalt carbonate hydroxide

Commerically available Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, NH<sub>4</sub>HCO<sub>3</sub>, and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> were used as reagents in the synthesis. First, 20 mmol of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 200 mmol of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> were dissolved in 700 mL of distilled water, yielding solution A. At the same time, 200 mmol of NH<sub>4</sub>HCO<sub>3</sub> was dissolved in 700 mL of distilled water, forming solution B. Then, 100 mL of ethanol was added to solution A under vigorous stirring, after which solution B was introduced. The resulting mixture was stirred in a water bath for 24 h at room temperature for sample 1 (S1), 50 °C for sample 2 (S2), and 80 °C for sample 3 (S3). The pink precipitates were collected by centrifugation and washed several times with distilled water and ethanol. Finally, the samples were dried at 60 °C over night.

### 2.2. Preparation of cobalt oxides

The precipitates were heated to 500 °C over 2.5 h and kept at this temperature for 3 h under either air or Ar. Heat treatment under air produced Co<sub>3</sub>O<sub>4</sub>, while treatment under Ar produced CoO. The obtained oxides were denoted as S1-Co<sub>3</sub>O<sub>4</sub>, S1-CoO, S2-Co<sub>3</sub>O<sub>4</sub>, S2-CoO, S3-Co<sub>3</sub>O<sub>4</sub>, and S3-CoO, respectively.

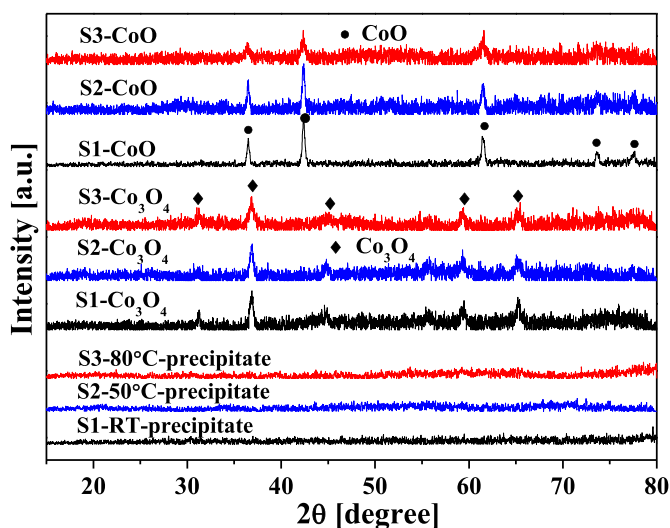


Fig. 2. XRD patterns for the precipitated precursors and cobalt oxide samples.

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