

## Research Article

# Synthesis of Hierarchical CoO Nano/Microstructures as Anode Materials for Lithium-Ion Batteries

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Hierarchical CoO nano/microstructures are synthesized via a hydrothermal method and a subsequent annealed process. When evaluated for use in lithium-ion batteries, hierarchical CoO nano/microstructures show a high initial discharge capacity of 1370 mAh/g and a high reversible capacity of 1148 mAh/g over 20 cycles at a current density of 100 mA/g. Superior rate performance with coulombic efficiency of about 100% upon galvanostatic cycling is also revealed. The excellent electrochemical properties of hierarchical CoO nano/microstructures make it a promising alternative anode material for high power lithium-ion batteries applications.

## 1. Introduction

The ever-increasing demands for the high power rechargeable lithium-ion batteries (LIBs) have been propelling the researches on the high performance electrode materials [1, 2]. The commercialized graphite-based anode materials exhibit excellent charge and discharge cycling performance, but their low specific capacities are far from the requirement of the high energy LIBs [3]. Recently, transition metal oxides (MO, where M refers to Co, Fe, Ti, or Ni) have aroused intense interests in the field of LIBs since their high electrochemical capacities were first reported by Poizot et al. [4]. Different from the classical intercalation reaction, the conversion reaction mechanism is adopted in transition metal oxides for the lithium-ion storage [5]. Theoretical and experimental investigations further demonstrate the occurrence of the multiple redox reaction between the transition metal oxides and lithium, which will lead to the high capacities in the transition metal oxides based LIBs [6–10].

Cobalt monoxide (CoO) with a relatively high theoretical capacity of 715 mAh/g is one of the potential candidate anode materials for rechargeable LIBs [11]. However, similar to other transition metal oxides anode materials, the poor cycle stability and rate capability of CoO anode materials hamper their large scale practical applications in LIBs [12–14]. Previous studies show that the poor electrochemical performance of

CoO anode materials is mainly due to the low conductivity and drastic volume change during lithiation/delithiation cycles [15, 16]. In recent years, considerable efforts have been devoted to overcome this drawback and an intuitively straightforward route is to decrease the size of the CoO anode materials to nanoscale [17–19]. Nanosized electrode materials with high specific surface may increase the contact area between the electrolyte and electrode materials and shorten the path length for Li ion transport during electrochemical reaction, which would do favor to the improvement of the discharge capacities [20–22].

In this paper, we report the synthesis of hierarchical CoO nano/microstructures via a hydrothermal method followed by a subsequent thermal annealing process. Hierarchical CoO nano/microstructures with the size of 5–7  $\mu\text{m}$  are consisting of many nanoparticles chains. The as-synthesized hierarchical CoO nano/microstructures exhibit a high initial capacity of about 1370 mAh/g and superior cycle stability. Good rate capability is also obtained in CoO nano/microstructures as anode materials for LIBs.

## 2. Experimental

The detailed synthesis process of hierarchical CoO nano/microstructures is described as follows. To begin, 1.50 g

(25 mmol) of urea and 0.05 g of cetyltrimethylammonium bromide (CTAB) are dissolved in 30 mL of deionized water under magnetic stirring. After the solution becomes transparent, 10 mL 0.5 M of  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  is added and stirred for another 10 minutes. Finally, the whole mixture is transferred into a Teflon-lined autoclave and maintained at  $120^\circ\text{C}$  for 12 h. When the autoclave is cooled to room temperature naturally, the rosy products are collected by filtration, rinsed several times with deionized water and absolute ethyl alcohol, and dried at  $60^\circ\text{C}$ . Finally, black CoO materials are obtained by thermal decomposition of the rosy precursor at  $500^\circ\text{C}$  for 2 h in a vacuum of  $10^{-5}$  torr.

The samples are characterized by X-ray powder diffraction (XRD, Philips X'pert PRO diffractometer,  $\text{Cu K}\alpha$  radiation), field emission scanning electron microscopy (FESEM, Hitachi S-4800, Japan), and high-resolution transmission electron microscopy (HRTEM, JEOL, 2010, 200 kV). To investigate the electrochemical properties of the as-prepared CoO hierarchical nano/microstructures, two-electrode coin-type cells are assembled with lithium metal as counter and reference electrodes. The working electrode was fabricated by spreading the mixture of CoO, acetylene black (ATB), and polyvinylidene fluoride (PVDF) in a weight ratio of 7:2:1 onto the copper foil. The electrode was then dried at  $120^\circ\text{C}$  for 2 h and cut into a disk. The electrolyte solution was 1 M  $\text{LiPF}_6$  dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) with the volume ratio of EC/DEC = 1:1. Cyclic voltammograms (CVs) test is conducted at room temperature, using the electrochemical workstation (CHI 660C) at a scan rate of 0.2 mV/s in a range of 0.01–3.0 V versus  $\text{Li/Li}^+$ . The rate capacity and the cycle performance are measured by a galvanostatic discharge-charge method at current densities of 100 mA/g, 200 mA/g, 300 mA/g, and 500 mA/g, respectively, in the range of 0.01–3.0 V with a multichannel battery test system (Land CT 2001A).

### 3. Results and Discussion

The crystalline phase of the as-prepared products was analyzed by XRD. Figure 1(a) shows the diffraction patterns for the products. All the characteristic diffraction peaks can be assigned to cubic CoO (JCPDS 78-0341,  $a = 4.2602 \text{ \AA}$ ). In addition, no additional diffraction peaks were detected, indicating the high purity of the CoO products. FESEM image (Figure 1(b)) illustrates the typical morphologies of the obtained CoO products. These CoO products are of hierarchical structures with diameters in the range of 5–7  $\mu\text{m}$ . Figure 1(c) represents the TEM image of a single CoO hierarchical structure, which is assembled from many nanosized branches radiating from a center. The HRTEM image (Figure 1(d)) further demonstrates that these radial nanosized branches are composed of numerous nanoparticles with the size of several nanometers. The measured lattice spacing of 0.216 nm corresponds to the (200) planes of cubic CoO.

Cyclic voltammogram (CV) measurements were carried out to investigate the electrochemical properties of the hierarchical CoO nano/microstructures as anode materials for

the LIBs. Figure 2 shows the first three CV curves at a scan rate of 0.2 mV/s in the range of 0.01–3.0 V. In the first cycle, a wide and irreversible reduction peak at about 0.20 V is observed, corresponding to the electrochemical lithiation reaction of the CoO and the formation of the solid electrolyte interface (SEI) layer. Previous studies reveal that the SEI layer might be formed on the surface of the transition metal oxides and results in the irreversible peak in the first CV curve [23, 24]. In the anodic scan process, a broad anodic peak is recorded at about 2.3 V, which is ascribed to the complex oxidation of metallic cobalt to cobalt oxide. The total chemical reaction can be expressed as  $\text{CoO} + 2\text{Li} \leftrightarrow \text{Li}_2\text{O} + \text{Co}$  [11]. The CV curve of the second cycle nearly overlaps with the curve for the third cycle, indicating the good cyclic stability of the CoO.

To investigate the lithium storage capacity, the galvanostatic discharge-charge performances were measured in the voltage window of 0.01–3.0 V at a current density of 100 mA/g. Figure 3 displays the 1st, 2nd, and 20th galvanostatic discharge-charge curves for the hierarchical CoO nano/microstructures. A long potential plateau at about 1.0 V, followed by a sloping curve down to the cutoff voltage of 0.01 V, is clearly observed from the first discharge curve. The long potential plateau could be ascribed to the conversion reaction between CoO and Li, while the sloping curve corresponds to the formation of the SEI layer [25]. The initial specific discharge capacity goes up to as much as 1370 mAh/g, which is much higher than its theoretical value of 715 mAh/g. The extra capacity could be ascribed to the formation of a polymer-gel-like film during the reduction process of CoO to Co and the formation of a  $\text{Co/Li}_2\text{O}$  interface in the course of the heterogeneous solid-state reaction process [26]. For the first charge, a voltage plateau at around 2.3 V is recorded, corresponding to the process of oxidation of metallic Co to CoO and the decomposition of the  $\text{Li}_2\text{O}$ , which is in accord with the CV measurement. The initial coulombic efficiency reaches 71.5% with the discharge and charge capacities of 1370 and 981 mAh/g, respectively. Compared to the initial discharge/charge curve, the discharge curves undergo a notable change in subsequent cycles, with shorter potential plateaus and longer sloping ranges. After the 20th cycle, the discharge and the charge capacities become 1148 and 1119 mAh/g, respectively, demonstrating the good capacity retention and cycle stability of the as-prepared hierarchical CoO nano/microstructures materials.

Figure 4 shows the discharge capacities of the as-prepared hierarchical CoO nano/microstructures as a function of the cycle number at different current densities. The CoO materials display a superior cyclic stability as well as high capacity. The initial discharge capacity is 1370 mAh/g at a current density of 100 mA/g. The discharge capacity of the 20th cycle is as high as 1144 mAh/g, which is 83.5% of the first discharge capacities. The rate performance of the hierarchical CoO nano/microstructures is also revealed, and the discharge capacities at 100 mA/g, 200 mA/g, 300 mA/g, and 500 mA/g are 1370 mAh/g, 1040 mAh/g, 822 mAh/g, and 593 mAh/g, respectively. Even under the high current density of 500 mA/g, the capacity of CoO is still higher than the theoretical capacity of commercial graphite anodes' materials

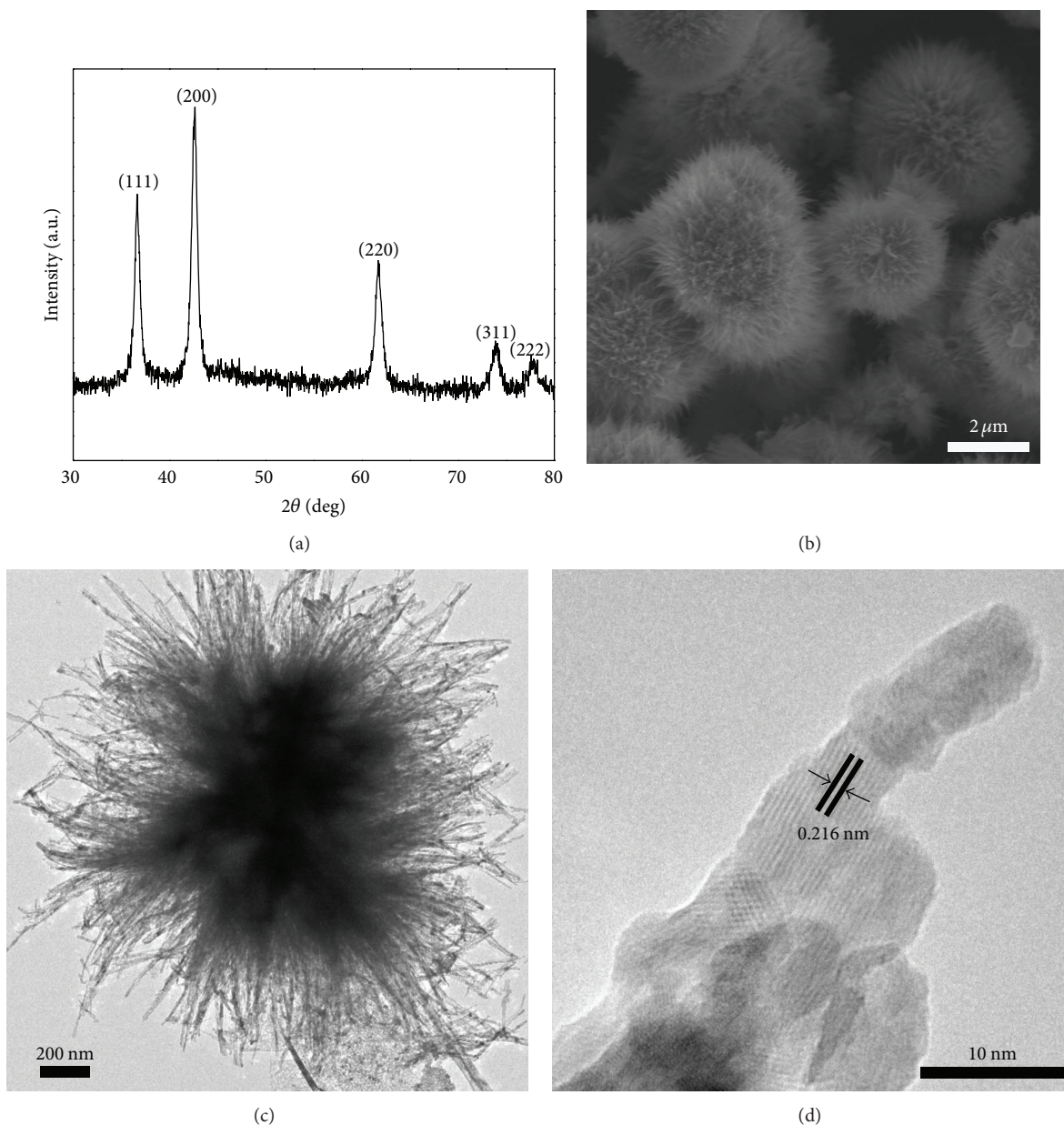


FIGURE 1: (a) XRD pattern of the as-prepared CoO products. ((b)–(d)) Characterization of hierarchical CoO nano/microstructures: (b) FESEM image, (c) TEM image, and (d) HRTEM image.

of 372 mAh/g. Moreover, when the current density reduces to 100 mA/g again, the capacity reaches back to 1054 mAh/g accordingly. The coulombic efficiency of the CoO is close to 100% during the cycles.

The superior electrochemical performance of the as-prepared hierarchical CoO nano/microstructures might originate from their unique nano/microstructures. The hierarchical CoO nano/microstructures with the size of several micrometers are composed of many CoO nanoparticles chains. The high specific surface of the CoO nanoparticles and the large porosity of the hierarchical nano/microstructures increase the contact area between the

electrolyte and CoO electroactive materials and shorten the path length for  $\text{Li}^+$  transport, improving the discharge capacity and the cycle stability of the CoO as anode materials for LIBs. Furthermore, the good rate performance of the CoO can be attributed to the electrochemical milling effect [27, 28], which can be observed in various metal oxides systems, including  $\text{Fe}_3\text{O}_4$  and  $\text{Cu}_2\text{O-Li}_2\text{O}$  composite electrodes.

#### 4. Conclusion

Hierarchical CoO nano/microstructures have been successfully synthesized by using a hydrothermal method and



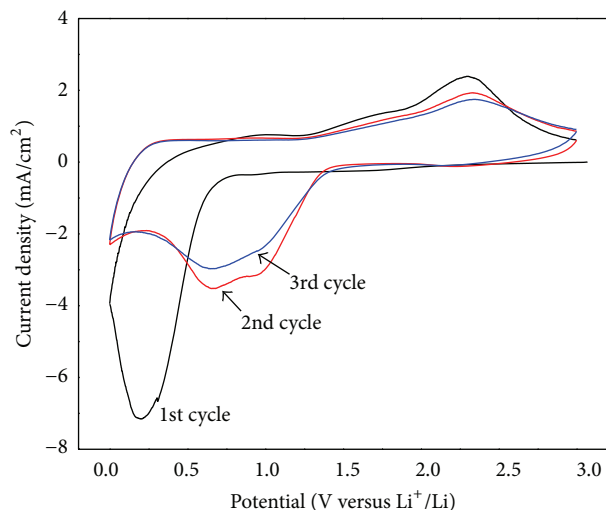


FIGURE 2: First three cyclic CV curves of the hierarchical CoO nano/microstructures at a scan rate of 0.2 mV/s.

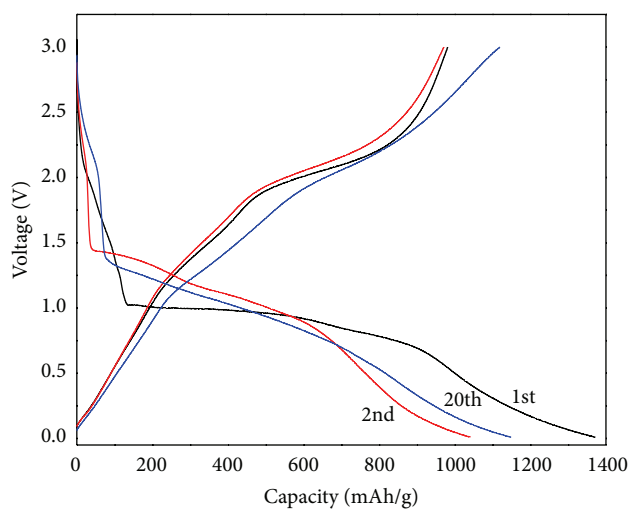


FIGURE 3: The galvanostatic discharge-charge profiles of the CoO electrode at a current density of 100 mA/g between 0.01 V and 3.0 V.

an annealing procedure. The as-prepared hierarchical CoO nano/microstructures exhibit superior electrochemical performance as anode materials for LIBs. A high discharge capacity of 1370 mAh/g and the retained discharge capacity of about 1144 mAh/g over 20 cycles are achieved at a current density of 100 mA/g. The excellent electrochemical performance might originate from these unique CoO nano/microstructures. Our works shed light on the extending applications of CoO as anode materials for high power LIBs.

### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

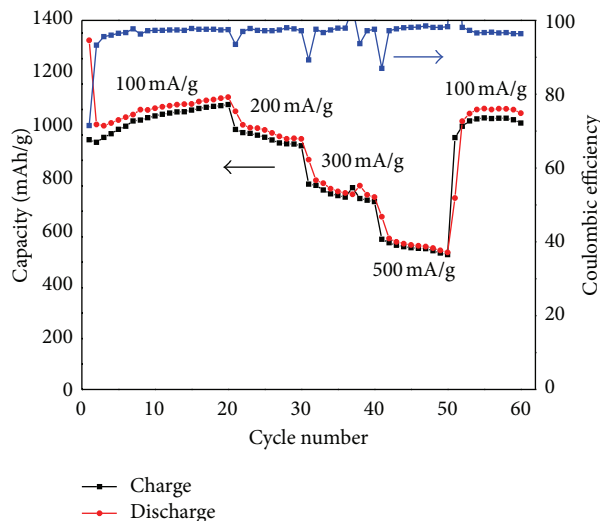


FIGURE 4: The specific capacity and the coulombic efficiency of CoO electrode under different current densities (100–500 mA/g).

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