# One-Dimensional Arrays of Co<sub>3</sub>O<sub>4</sub> Nanoparticles: Synthesis, Characterization, and Optical and Electrochemical Properties

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One-dimensional arrays of  $Co_3O_4$  nanoparticles were obtained via the thermal treatment of cobalt oxalate nanorods, which were synthesized through a convenient solvothermal route. The optical properties of  $Co_3O_4$  nanoparticles were investigated. The optical absorption spectrum indicates that the direct band gaps of  $Co_3O_4$  nanoparticles are 1.52 and 2.01 eV. The galvanostatic experiment shows the excellent electrochemical performance between 3.0 and 0.2 V.

## Introduction

There has been an increasing interest in developing materials based on cobalt oxides because of their potential application in many technological fields.<sup>1–4</sup> Co<sub>3</sub>O<sub>4</sub> belongs to the normal spinel crystal structure based on a cubic close packing array of oxide ions, in which Co(II) ions occupy the tetrahedral 8a sites and Co(III) ions occupy the octahedral 16d sites.<sup>5,6</sup> In recent years, Co<sub>3</sub>O<sub>4</sub> has been extensively investigated in view of their application as gas sensors,<sup>7,8</sup> catalysts,<sup>9–11</sup> magnetic materials,<sup>12</sup> electrochromic devices,<sup>13</sup> and high-temperature solar selective absorbers.<sup>14–16</sup>

Nanomaterials with the size of 1-100 nm have attracted considerable interest due to the departure of properties from bulk phases arising from quantum size effect. Therefore, much effort has been made to prepare cobalt oxide nanoparticles, including sol-gel,<sup>17</sup> reduction/oxidation route,<sup>18</sup> homogeneous precipitation,<sup>19</sup> and metal organic chemical vapor deposition (MOCVD).<sup>20,21</sup> It is well-known that the behaviors of nanophase materials strongly depend on the shapes and sizes of the particles, which are thus a key factor to their ultimate performance and applications. In this Article, one-dimensional (1D) arrays of Co<sub>3</sub>O<sub>4</sub> nanoparticles were synthesized by the thermal treatment of the rodlike cobalt oxalate precursor at 420 °C. The optical absorption properties and the electrochemical performance of the Co<sub>3</sub>O<sub>4</sub> nanoparticles were investigated.

### **Experimental Section**

All the reagents are of analytical purity grade and have been received from commercial sources. In a typical synthesis, Co- $(CH_3COO)_2 \cdot 4H_2O$  (2 mmol) was dissolved into 10 mL of absolute ethanol to form a homogeneous solution. A stoichiometric amount of oxalic acid dissolved in an equal volume of ethanol was dropwise added into the above solution under magnetic stirring. Then the suspension colloids were transferred into a Teflon-lined stainless steel autoclave, which was filled with ethanol up to 80% of the total volume, sealed, and heated at 120 °C for 12 h. The obtained solid product was centrifuged, washed with absolute alcohol and distilled water, and dried at

80 °C under vacuum. Finally, for  $Co_3O_4$ , part of the obtained cobalt oxalate was heated to 420 °C for 2 h at a heating rate of 5 °C/min.

### Characterization

The crystalline phase was identified by X-ray diffraction (XRD) using a Philips X'Pert Pro Super diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.541784$  Å). The morphologies of the samples were examined by transmission electron microscopy (TEM, Hitachi, Model H-800) with an accelerating voltage 200 kV. Thermal gravimetric analysis (TGA) of the as-synthesized sample was carried out on a Shimadzu TA-50 thermal analyzer at a heating rate of 10 K min<sup>-1</sup> from room temperature to 800 °C in air. X-ray photoelectron spectrum (XPS) was collected on an ESCALab MKII X-ray photoelectron spectrometer, using nonmonochromatized Mg K $\alpha$  X-ray as the excitation source and C 1s (284.6 eV) as the reference line. Optical absorption spectrum was recorded on a Shimadzu UV-2401PC UV-vis recording spectrophotometer.

The performance of the Co<sub>3</sub>O<sub>4</sub> as cathode was evaluated using a Teflon cell with a lithium metal anode.<sup>22</sup> The cathode was a mixture of Co<sub>3</sub>O<sub>4</sub>/acetylene black/poly(vinylidene fluoride) (PVDF) with weight ratio 85/10/5. The electrolyte was a 1 M LiPF<sub>6</sub> in a 1:1 mixture of ethylene carbonate (EC)/diethyl carbonate (DEC), and the separator was Celgard 2500. The cell was assembled in the glovebox filled with highly pure argon gas (O<sub>2</sub> and H<sub>2</sub>O levels < 5 ppm). The galvanostatic charge/ discharge experiment was performed between 3.0 and 0.2 V at constant discharge rates ranging from 1 lithium per formula unit in 5 h (1 Li<sup>+</sup>/5 h) to 1 Li<sup>+</sup>/h.

#### **Results and Discussion**

Figure 1 shows the XRD patterns of the as-prepared cobalt oxalate precursor and Co<sub>3</sub>O<sub>4</sub> nanoparticles. All the diffraction peaks of Figure 1a show characteristics of the cobalt oxalate hydrate phase, which is in good agreement with the reported compound,  $\beta$ -Co(COO)<sub>2</sub>·xH<sub>2</sub>O, with lattice parameters a = 11.87, b = 5.419, and c = 15.62 Å (JCPDS: 25-0250).

The TGA curve of the cobalt oxalate nanorods is shown in Figure 2. There are two weight loss steps at the temperature ranges 30-210 and 210-400 °C. The first weight loss is mainly

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Figure 2. TGA curve of the cobalt oxalate compound.

attributed to the evaporation of  $H_2O$ , whereas the second one may be ascribed to the decomposition of the oxalate. The weight loss during the second step is about 38.35%, which is close to the theoretical value.

Upon the calcination of the obtained oxalate nanorods at 420 °C in air, all the cobalt oxalate was converted into  $Co_3O_4$  nanoparticles. The XRD pattern of the calcined sample is shown in Figure 1b. All the reflection peaks can be indexed to a pure cubic phase of  $Co_3O_4$  spinel with lattice parameter a = 8.076 Å, which is consistent with the reported value (a = 8.083 Å) (JCPDS: 42-1467). Evaluated from the Debey–Scherrer formula, the average particle size is about 35 nm. No other peaks for impurities were detected.

The TEM images of the oxide and the precursor are shown in Figure 3. From the images of cobalt oxalate (Figure 3a,b), a rodlike morphology with an average diameter of 50 nm and an average length of 2  $\mu$ m is observed. As shown in Figure 3c,d, one-dimensional arrays of Co<sub>3</sub>O<sub>4</sub> nanoparticles interconnected along the original directions of the oxalate nanorods are observed. The observed average particle size is about 40 nm, which is consistent with the XRD result. The strings of Co<sub>3</sub>O<sub>4</sub> nanoparticles could be ascribed to the shape confinement of the precursors and the formation of a layer of ferromagnetic Co on the oxide surface under the TEM electron beam, which may cause a self-alignment of the small particles through weak magnetic interactions. XPS has been widely used in the characterization of materials. The Co 2p core spectrum is shown



Figure 3. TEM images of the rodlike cobalt oxalate precursor (a, b) and the 1D arrays of  $Co_3O_4$  nanoparticles (c, d).



Figure 4. High-resolution XPS core spectrum for Co 2p in the oxide sample.

in Figure 4. The two strongest peaks at 780.5 and 795.7 eV correspond to Co  $2p_{3/2}$  and Co  $2p_{1/2}$ , respectively, characteristic of the Co<sub>3</sub>O<sub>4</sub> phase.<sup>23</sup> All the results comfirm the formation of the pure Co<sub>3</sub>O<sub>4</sub> nanoparticles.

Figure 5a shows the optical absorption spectrum of the  $Co_3O_4$  nanoparticles. The absorption band gap  $E_g$  can be determined by the following equation:

$$(\alpha h\nu)^n = B(h\nu - E_g) \tag{1}$$

where  $h\nu$  is the photo energy,  $\alpha$  is the absorption coefficient, *B* is a constant relative to the material, and *n* is either 2 for a direct transition or 1/2 for an indirect transition. The  $(\alpha h\nu)^2 \sim$ 



Figure 5. Optical absorption spectrum (a), and  $(\alpha h\nu)^2 \sim h\nu$  curve (b) for the Co<sub>3</sub>O<sub>4</sub> nanoparticles



Figure 6. Voltage versus discharge capacity curves for the Co<sub>3</sub>O<sub>4</sub>/Li cell between 3.0 and 0.2 V at different discharge rates: (a) 1 Li<sup>+</sup>/5 h, (b) 1 Li<sup>+</sup>/3 h, and (c) 1 Li<sup>+</sup>/h. Inset: the cyclic performance of the nanoparticles cycled at 1 Li<sup>+</sup>/5 h at room temperature.

 $h\nu$  curve for the sample is shown in Figure 5b, exhibiting a linear relationship at 1.5–1.6 and 2.0–2.3 eV, respectively. The band gaps of the Co<sub>3</sub>O<sub>4</sub> nanoparticles are 1.52 and 2.01 eV by the extrapolation of eq 1, which are in good agreement with the reported values for Co<sub>3</sub>O<sub>4</sub>.<sup>21,24,25</sup> No linear relation was found for  $n = \frac{1}{2}$ , suggesting that the as-prepared Co<sub>3</sub>O<sub>4</sub> nanoparticles are semiconducting with direct transitions at these energies.

Electrochemical properties of the as-prepared  $Co_3O_4$  in the cell configuration  $Co_3O_4/Li$  have been investigated at room temperature. Figure 6 shows the voltage versus capacity for the cell between 3.0 and 0.2 V at different discharge rates. The discharge capacity of ca. 1150 (mA h)/g can be obtained at 1 Li<sup>+</sup>/5 h, corresponding to intercalation of 10 lithium per formula unit. The contribution of the reaction of lithium with carbon additive is at a magnitude of 60 (mA h)/g, and is thus not taken inton account for such high specific capacity. With increasing discharge rate, the well-developed potential plateau shifts toward a slow sloping voltage, implying some kinetic limitations. The whole electrochemical reaction can be written as follows:

$$\text{Co}_3\text{O}_4 + 8\text{Li}^+ + 8\text{e}^- \frac{\text{discharge}}{\text{charge}} 3\text{Co} + 4\text{Li}_2\text{Co}$$

The extra capacity can be associated with the occurrence of a redox process involving the electrolyte.<sup>26,27</sup> Subsequently, almost eight lithium can be reversibly intercalated/deintercalated. The



Figure 7. Voltage versus discharge capacity curve and the cycle performance (inset) for the bulk  $Co_3O_4$  at 1 Li<sup>+/5</sup> h at room temperature.

inset of Figure 6 shows the cyclic performance of the sample cycled at 1 Li<sup>+</sup>/5 h at room temperature. The sample exhibits excellent cyclability. The reversible capacity after 11 cycles is 841 (mA h)/g (95% of the second discharge capacity). The nanostructured cobalt oxide, as a promising negative-electrode material, has about twice the capacity of carbon per unit mass, and 3 times its density, and therefore has about 6 times the capacity of carbon per unit volume.

It has been identified that the size and morphology of the precursor particles have a crucial effect on the electrochemical behavior of these metal oxides toward lithium.<sup>28,29</sup> So we also investigated the electrochemical performances of the bulk Co<sub>3</sub>O<sub>4</sub>. Figure 7 shows the discharge curve and the cycle life of the bulk one. It delivered the first discharge capacity of about 822 (mA h)/g and then decreased down to 372 (mA h)/g after the second cycle. Subsequently, the discharge capacity of the bulk one appeared to increase slightly due to the crystal perfection, which usually proceeds with the activation process for electrochemical reaction of lithium. The improved electrochemical performances of the as-prepared Co<sub>3</sub>O<sub>4</sub> nanoparticles may be ascribed to the unique microstructure and smaller particle size achieved by the present synthesis procedure. With decreasing particle size, an increasing proportion of the total number of atoms lies near or on the surface, making the electrochemical reactivity of the particles more and more important and facilitating the intercalation/deintercalation of lithium ions.

#### Conclusion

In summary, one-dimensional arrays of  $Co_3O_4$  nanoparticles were successfully synthesized by the thermal treatment of the rodlike cobalt oxalate precursor at 420 °C. And the optical absorption properties of the  $Co_3O_4$  nanoparticles were investigated. The results indicate that the nanoparticles are semiconducting with direct transitions at 1.52 and 2.01 eV. The galvanostatic experiment shows the excellent electrochemical performance between 3.0 and 0.2 V. The nanostructured cobalt oxide, as a promising negative-electrode material, has about twice the capacity of carbon per unit mass, and 3 times its density, and therefore has about 6 times the capacity of carbon per unit volume.

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#### **References and Notes**

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