Over the past decades, a worldwide effort has been made to search for alternative anode materials of lithium batteries for improving their energy density and safety. It has been found that 3d transition metal oxides such as nickel oxide, cobalt oxide, and iron oxide exhibit reversible capacities about three times larger than those of graphite (372 mAh g⁻¹) at a relative low potential, which greatly spurs the rapid development in this field. Among them, cobalt oxides (Co₃O₄ and CoO) have shown the highest capacity (700 mAh g⁻¹) and best cycle performance (93.4 % of initial capacity was retained after 100 cycles), compared with nickel oxide (NiO) and iron oxides (Fe₂O₃ and Fe₃O₄). In recent years, the nanostructured materials have attracted great interest in the application of anode or cathode materials for lithium batteries because of their high surface-to-volume ratio and short path length for Li⁺ transport. As a result, it is believed that the Co₃O₄ nanomaterials can exhibit the superior Li-battery performance.

Previously, several Co₃O₄ nanostructures such as nanoparticles, nanowires, and nanotubes were prepared by different methods. One of the most promising structures for lithium batteries due to their high surface-to-volume ratio than other one-dimensional nanostructures such as nanowires and more difficult for aggregation in comparison with nanoparticles. By far, there is little literature about the synthesis and application of Co₃O₄ nanotubes for lithium batteries. For example, Chen et al. synthesized the Co₃O₄ nanotubes via the anodic aluminum oxide (AAO) template route and applied them for lithium batteries with the capacity of about 800 mAh g⁻¹ at the current density of 50 mA g⁻¹. However, there are some disadvantages for the AAO template assisted approach to synthesize metal oxide nanotubes, which restrict their application in Li-battery. Firstly, the mass production of metal oxide nanotubes prepared by such an approach is impracticable, which is one of the bottlenecks for their wide applications. Secondly, it is very difficult to completely remove the nanoporous alumina template. Thirdly, the diameters of metal oxide nanotubes prepared by such an approach are usually larger than 100 nm.

Recently, carbon nanotubes (CNTs) have been considered to be an ideal template for the synthesis of metal oxide nanotubes due to the mass production, being easily removed and small diameter. For example, Liu et al. reported the synthesis of Fe₂O₃/CNTs core-shell nanostructures and polycrystalline Fe₂O₃ nanotubes by supercritical fluids approach using CNTs as templates. Unfortunately, the high temperature and pressure were needed in this approach. In addition, metal oxide/CNTs core-shell nanostructures and metal oxide nanotubes were also achieved by CNT-template assisted chemical vapor deposition (CVD), which operated at high temperature and, moreover, only deposited oxides on the top surface of CNTs. Furthermore, metal oxide/CNTs core-shell nanostructures were also fabricated by chemical precipitation method. However, the formation of metal oxide nanoparticles in the solution or metal oxide with very large grain size on the surface of CNTs was inevitable in this approach, which made it difficult to form metal oxide nanotubes after oxidation of CNTs. Very recently, we have developed a novel approach to synthesizing the porous and polycrystalline In₂O₃ nanotubes by layer-by-layer assembly on CNT templates in combination with subsequent calcinations, which exhibit superior gas sensing performance. Herein, we report a novel sonochemistry method to synthesizing CNTs-CoO₃ nanocables derived from Co₄(CO)₁₂ clusters on CNT templates at room temperature and subsequent transformation into uniform porous Co₃O₄ nanotubes by the calcination. Moreover, the as-synthesized porous Co₃O₄ nanotubes have been applied in anode materials for lithium batteries, which exhibit the superior performance and thus promising application.
with negative charge after nitric acid treatment due to the 
electrostatic attraction between the charged species. With the 
extension of the reaction time, the shell layer of CoO$_x$ was 
formed on the surface of CNTs. Finally, the porous Co$_3$O$_4$ 
nanotubes were obtained by the calcination (the detailed 
growth condition can be seen in the Experimental section).

\[ \text{Co}_4(\text{CO})_{12} \rightarrow 4\text{Co} + 12\text{Co} \]  \hspace{1cm} (1)

\[ \text{Co} + \text{O}_2 \rightarrow \text{CoO}_x \]  \hspace{1cm} (2)

Figure 1 shows the morphological and structural characteri-
zations of the products prepared by the sonication for 1h at 
room temperature in the hexane solution of Co$_4$(CO)$_{12}$ and 
CNTs. As can be seen from the transmission electron micros-
copy (TEM) image (Fig. 1a), almost all CNTs have been fully 
coated with the thin and uniform layers. The occasional bro-
ken place marked by an arrow in Figure 1b clearly confirms 
the formation of CNT-CoO$_x$ nanocables. The high-resolution 
transmission electron microscopy (HRTEM) performed on an 
individual CNT-CoO$_x$ nanocable, as illustrated in Figure 1c, 
indicates that the thickness of the shell is usually less than 
10 nm. Moreover, no observation of the lattice fringe from 
the part of the CoO$_x$ shell in the HRTEM image reveals that 
the as-synthesized CoO$_x$ shell is amorphous. In addition, the 
thickness of the CoO$_x$ shell can be readily regulated by the ra-
tio of CNTs to Co$_4$(CO)$_{12}$. The energy dispersive X-ray
(EDX) analysis of the nanocables is shown in Figure 1d. The 
strong peaks for Co, O and C are found in the spectrum, 
which corresponds to CNTs and CoO$_x$. While, the Cu peak 
comes from the Cu grid used for TEM measurements.

It has been reported that CNTs can be oxidized into CO$_2$
above 400 °C.[14] Therefore, after the calcination at 500 °C in 
O$_2$, the CNTs can be completely removed and the amorphous 
CoO$_x$ shell can be oxidized and crystallized. Figure 2a shows 
the XRD pattern of the sample after the calcination. All the 
diffraction peaks can be indexed as cubic Co$_3$O$_4$ with the lat-
tice constants $a = 8.08$ Å, which are consistent with the values 
in the standard card (JCPDS Card No.42-1467). No peaks from 
other phases have been detected. Moreover, the morphological 
coloration of the sample after the calcination is displayed 
in Figure 2b and c. From those images, a large quantity of the 
uniform Co$_3$O$_4$ nanotubes with the diameter of about 30 nm 
can be observed. The magnified TEM image (Fig. 2d) reveals

Figure 1. Morphological and structural characterizations of CNTs-CoO$_x$ nanocables prepared by the sonication for 1h at room temperature in the hex-
ane solution of Co$_4$(CO)$_{12}$ and CNTs: a) TEM image; c) HRTEM image; d) EDX pattern.
that the wall thickness of the nanotubes is about 5 nm. Furthermore, there are lots of pores with the size of about several nanometers in the wall of the nanotubes due to the decomposition of CNTs, which greatly improves the surface-to-volume ratios of Co3O4. The inset in Figure 2d shows the HRTEM image of an individual Co3O4 nanotube. From this image, the Co3O4 nanotube is composed of nanoparticles with the size of about 5–10 nm, indicating that the Co3O4 nanotubes are polycrystalline in nature. Moreover, the lattice fringes with a lattice spacing of about 0.467 nm corresponds to the {111} planes of Co3O4, which is consistent with the XRD results.

It has been proved that the electrochemical reaction mechanism of Li with transition metal oxides such as Co3O4 differs from the classical mechanisms, which are based either on reversible insertion/deinsertion of lithium into host structures or on lithium alloying reactions.13,15 Therefore, the electrochemical reaction mechanism of Li with porous Co3O4 nanotubes in Li-battery can be described as follows:

$$\text{Co}_3\text{O}_4 + 8\text{Li}^+ + 8\text{e}^- \leftrightarrow 4\text{Li}_2\text{O} + 3\text{Co}^0$$  (3)
$$8\text{Li} \leftrightarrow 8\text{Li}^+ + 8\text{e}^-$$  (4)
$$\text{Co}_3\text{O}_4 + 8\text{Li} \leftrightarrow 4\text{Li}_2\text{O} + 3\text{Co}^0$$  (5)

Figure 3a shows the first three cyclic voltammogram (CV) curves of the electrodes made from the porous Co3O4 nanotubes at a scan rate of 0.5 mVs–1 and a temperature of 20 °C. The first discharge for the porous Co3O4 nanotubes shows an irreversible reduction peak with a maximum at 0.4 V, which is different from the previous result due to the incomplete decomposition of Co3O4.16 Compared to the first cycle, the discharge of the second and third cycles shows two peaks during cathodic polarization process attributed to two complete multistep redox reactions. While, in the anodic polarization process, one peak is recorded at about 2.2 V corresponding to oxidation of Co0 to Co3+. Figure 3b shows the 1st, 10th, and 20th discharge curves of the electrodes made from the porous Co3O4 nanotubes at a current density of 50 mA g–1 and a temperature of 20 °C. In the first discharge curve, it can be seen that there are two sloping potential ranges for the lithium reaction during the first potential discharge, which is similar to the previous report.6 During the 10th and 20th cycles, only one discharge slope is observed in the range (0.7–1.3V), with a decrease of the discharge capacity. The discharge capacities of the electrode in the 1st, 10th, and 20th cycles are 1918, 1269, and 1131 mAh g–1, respectively.

Figure 4 shows the discharge capacity versus cycle number for the electrodes made from the porous Co3O4 nanotubes. Except the first cycle (about 1918 mAh g–1), the capacity of other nineteen cycles is almost maintained constant at about 1200 mAh g–1, which shows the high capacity and good cycle life. To our best knowledge, the performance of the Co3O4 based anode materials for lithium batteries presented here is the best up to now.4a,6 The porous nanotube structures with the diameter of 30 nm consisting of the small nanoparticles

Figure 2. Morphological and structural characterizations of the Co3O4 nanotubes prepared by the calcination of CNT-CoO nanocables at 500 °C in O2 for 3 h: a) XRD pattern; b) FESEM image; c), d) TEM image. The upper-left inset in d corresponds to the HRTEM image.
with the size of about 5–10 nm are responsible for the improved performance. However, the initial coulombic efficiency for the porous Co$_3$O$_4$ nanotubes is only about 70 %, which is similar to the previous reports[15–17]. It was considered that the formation of the solid electrolyte interface (SEI) film and some undecomposed Li$_2$O phase were responsible for the low initial coulombic efficiency.[16,17] In this paper, TEM image (Figs. S1a, S1b) and XRD pattern (Fig. S1c) of the porous Co$_3$O$_4$ nanotube electrode taken from the first cycle indicate that the morphology and structure have been basically maintained after the first charge and discharge processes, which correspond to the previous reports.[7,16,17] Moreover, the Fourier transform infrared (FTIR) spectroscopy, as shown in Figure S1d, confirms the existence of Li$_2$CO$_3$ and ROCO$_2$Li, which are the main components of SEI film. Therefore, it is believed that the formation of the SEI film may be the main reason for the low initial coulombic efficiency of the porous Co$_3$O$_4$ nanotube electrode.

In summary, we have developed a novel and simple method to synthesizing the porous Co$_3$O$_4$ nanotubes with the diameter of about 30 nm consisting of the small nanoparticles with the size of about 5–10 nm by the sonication in the hexane solution of Co$_4$(CO)$_{12}$ using CNTs as templates at room temperature and the subsequent calcination. The approach presented here can overcome the disadvantages of the AAO assisted method for the synthesis of the porous nanotubes, make it more suitable for Li-battery application. Moreover, the porous Co$_3$O$_4$ nanotubes exhibit the superior Li-battery performance with good cycle life and high capacity (1200 mAh g$^{-1}$) due to the hollow structure and small size.

**Experimental**

The carbon nanotubes (CNTs) with the diameter of about 30–50 nm were purchased from Times-nano Nanotech Co. Ltd. without further purification. Co$_4$(CO)$_{12}$ were purchased from Alfa Aesar China (Tianjin) Co. Ltd. The experimental details were as follows: Firstly, the CNTs were dispersed in hexane by the sonication for 1 h. Secondly, appropriate quantity of Co$_4$(CO)$_{12}$ were directly added into the above-mention solution and sonicated for 0.5 h. After the reaction completed, the resulted products were centrifugalized, washed with deionized water and ethanol to remove the ions possibly remaining in the final product, and dried at 60 °C in air. Finally, the black powder was calcinated at 500 °C in oxygen for 3 h.

The product was characterized by X-ray powder diffraction (XRD) using a Rigaku D/Max-ga x-ray diffractometer with graphite monochromatized CuKα radiation (λ = 1.54178 Å). The images and structures of the sample were obtained by field emission scanning electron microscopy (FESEM, FEI SIRION), transmission electron microscopy (TEM, JEM 200 CX 160 kV) and high-resolution transmission electron microscope (HRTEM, JEOL JEM-2010F).

Electrochemical measurements were carried out using two-electrode cells with lithium metal as the counter and reference electrodes. The working electrodes were composed of the active material (Co$_3$O$_4$ nanotubes), conductive material (acetylene black, ATB), and binder (polytetrafluoroethylene, PTFE) in a weight ratio of Co$_3$O$_4$/ATB/PTFE = 14:3:3. The electrode was dried at 80 °C for 1h and cut into a disk (1.0 cm$^2$). The electrolyte solution was 1M LiPF$_6$ dissolved in a mixture of ethylene carbonate (EC), propylene carbonate (PC), and
diethyl carbonate (DEC) with the volume ratio of EC/PC/DEC = 3:1:1. The cell assembly was performed in a glove-box filled with pure argon (99.999 %) in the presence of an oxygen scavenger and a sodium drying agent. The electrode capacity was measured by a galvanostatic discharge-charge method at a current density of 50 mA g⁻¹ and 20 °C. Charge-discharge cycles were tested with a current density of 50 mA g⁻¹ in the potential range of 0.01–3.6V.

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