# Multiwalled Carbon Nanotubes/$Co_3O_4$ Nanocomposites and Its Electrochemical Performance in Lithium Storage

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Multiwalled carbon nanotubes (MWNTs) coated with a thick layer of $Co_3O_4$ nanocrystals were prepared through a facile and effective method for the first time, which combined the acid treatment MWNTs and in situ decomposition of $Co(NO_3)_2$ in *n*-hexanol solution at 140 °C. TEM images show that the MWNTs are nearly fully coated with a layer of $Co_3O_4$ with an average size of 8 nm. The coating layer is 15–20 nm in thickness. The electrochemical performance in $Li^+$ insertion and extraction reactions shows that the MWNTs/$Co_3O_4$ composites have larger lithium storage capacities and a better cycle-ability.

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Carbon nanotubes (CNTs) have been one of the focuses of intensive study because of their unique structure and physical properties. They are thought to have potential applications as catalyst supports, structure reinforcements, Li-ion batteries materials, and nanoelectronic devices, etc.[1] For most of these applications, the highly dispersive and surface functionalized CNTs are desirable. It has been demonstrated that the physical properties of CNTs can be dramatically influenced by surface modification with selected organic, inorganic, and biological species.[2] Such functionalization can lead to a great improvement of properties relevant to technological applications. So CNTs coated with nanolayers of different materials will open a new era of nanotechnology research and the fabrication of 'smart' composite materials. To optimize the use of CNTs in various applications, it is necessary to attach functional groups or nanostructures to nanotubes.[3]

Recently, increasing attentions have been paid to coating CNTs with inorganic materials. Surface coverage with a layer or nanoparticles of $SiO_2$,[4] $Al_2O_3$,[3,5] $SnO_2$,[6] ZnS,[7] $TiO_2$,[8] and some metals have been widely reported. Spinel $Co_3O_4$ is an important magnetic p-type semiconductor that has been widely used as solid-state sensors, heterogeneous catalysts, supercapacitors, Li-ion rechargeable batteries, ceramic pigments and electrochromic devices.[9–13] Such a broad perspective of utilization makes the preparation of $Co_3O_4$ nanostructure much more attractive.[14–16] However, to the best of our knowledge, there are no reports about carbon nanotube–$Co_3O_4$ composites by far. Herein we demonstrated a simple and effective method of in situ coating MWNTs with a thick layer of $Co_3O_4$ nanocrystals using ordinary $Co(NO_3)_2{\cdot}6H_2O$ as the metal ion source and without adding any surfactants.

MWNTs prepared by the catalytic decomposition of $CH_4$ were kindly provided by Shenzhen Nanoport Company. They were dried at 140 °C for 24 h before use. A typical experimental procedure was described as follows. Firstly, the dried MWNTs were treated by concentrated nitric acid (AR grade) at 140 °C for 6 h according to the procedure described in literature.[17] Then the treated MWNTs were rinsed with distilled water and dried at 100 °C for 12 h. Secondly, 0.5 g of $Co(NO_3)_2{\cdot}6H_2O$ was dissolved into 40 mL of *n*-hexanol to form a red solution. 150-mg of acid treated MWNTs was dispersed in the red solution by ultrasonication for 2 h. After that, this solution was refluxed at 140 °C for 10 h. After cooled to ambient temperature, the products were washed with cyclohexane repeatedly to remove any impurities and dried. A series of MWNTs/$Co_3O_4$ composites with different content of MWNTs were prepared, and the samples were denoted as C–$Co_3O_4$-$x$%. ($x$ is the weight percent of MWNTs). The composites were characterized by XRD (D/MAX 2550V Rigaku, Japan), TEM (JEOL 200CX, Japan). The electrochemical performance of Li batteries was recorded by a LAND CT2001A battery tester with Li/(MWNTs coated with $Co_3O_4$) button cells including a lithium metal foil as counter electrode, MWNTs coated with $Co_3O_4$ composites as cathode.

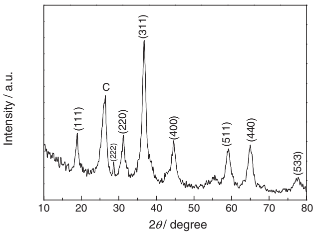

**Figure 1.** XRD pattern of the MWNTs–$Co_3O_4$ composites.

Figure 1 shows the XRD pattern of the MWNTs/$Co_3O_4$ composites. Except the peak at $2\theta = 26°$, which is corresponding to the (002) reflection of the MWNTs, all the other peaks belong to the characteristic peaks of spinel $Co_3O_4$, which are close to the values on JCPDS card (No. 431003) with the lattice constant of $a = 8.083$ Å. The broad peaks of $Co_3O_4$ in the XRD pattern indicate that the nanoparticles are small, and the average size of $Co_3O_4$ calculated by Scherrer equation is ≈8 nm. The unchanged MWNTs (002) peak position indicates that the $Co_3O_4$ coating does not cause much distortion of the MWNTs' shell. No obvious peaks corresponding to other cobalt oxide are observed.

Figure 2 shows the typical TEM images of the MWNTs (a) before, (b) after, and (c) coated with $Co_3O_4$. It can be seen that the pristine MWNTs have lengths ranging from several to tens of micrometers with inner diameter around 10 nm and outer diameter 50 nm. After fully coated with a thick layer of $Co_3O_4$ nanocrystals, the outer diameter is around 90 nm. The coating layer is estimated around 15–20 nm in thickness, and is composed of $Co_3O_4$ with size of less than 10 nm, which is consistent with the XRD results. The coating of the individual MWNTs is nearly uniform except a few segregated $Co_3O_4$ nanocrystals conglomerate on the $Co_3O_4$-coating layer as the arrow shown in Figure 2c. Also a few dissociative 20–40 nm $Co_3O_4$ aggregated balls are found as the arrow shown in Figure 2b, which is due to the $Co_3O_4$

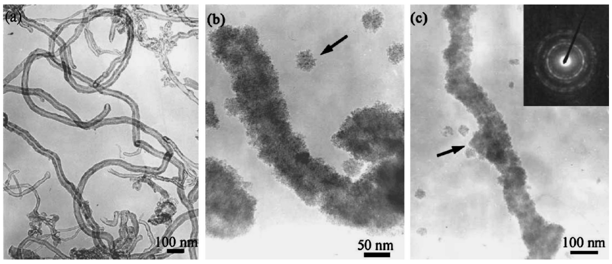

**Figure 2.** TEM images of MWNTs (a) before, (b) after, and (c) coated with $Co_3O_4$, inset is the selected area electron diffraction pattern of $Co_3O_4$.

nanoparticles minimization their surface potential energy. The corresponding selected area electron diffraction patterns (SAED) taken from the selected regions of $Co_3O_4$ nanoparticles exhibit five rings corresponding to (220), (311), (400), (511), and (440) planes of $Co_3O_4$, respectively, which further confirms the existence of $Co_3O_4$ nanoparticles on the surface of MWNTs.

After oxidized with nitric acid, the surface of MWNTs possesses a great deal of functional carboxyl groups. The MWNTs are negatively charged[6] and become more hydrophilic. Cobalt ions in the hydrophobic *n*-hexanol solution are adsorbed to the surface of the nitric acid-treated MWNTs through electrostatic attraction and hydrophilic affinity, and then in situ decompose into $Co_3O_4$. In addition, on the one hand, cobalt ions continuously are adsorbed on the as-originated $Co_3O_4$-coating layer and slowly crystallize to $Co_3O_4$ nanoparticles; on the other hand, some $Co_3O_4$ nanoparticles crystalize in the solution, which either adsorb on the as-originated $Co_3O_4$-coating layer or congregate into agglomerates, just as the arrow shown in Figure 2b. These might be why MWNTs can be thickly coated with $Co_3O_4$.

The first discharge-charge curves of MWNTs, $Co_3O_4$, and C–$Co_3O_4$-10% composite electrodes are shown in Figure 3. It can be seen that $Co_3O_4$ is an active material towards Li storage, whose Li-insertion and Li-extraction capacity of $Co_3O_4$ reaches 1100.5 and 682.7 $mA \cdot h \cdot g^{-1}$, repectively. The Li-insertion and Li-extraction capacity of MWNTs is only 313.7 and 217.6 $mA \cdot h \cdot g^{-1}$, but after being coated with $Co_3O_4$, its capacities in Li-insertion and extraction are 591.7 and 407.9 $mA \cdot h \cdot g^{-1}$, respectively, which are nearly two times as high as that of MWNTs. What's more, first cycle efficiency has been improved from 69% for MWNTs to 88.5% in C–$Co_3O_4$-10%.

A comparison of the cycle-ability of MWWNTs, $Co_3O_4$ and MWWNTs/$Co_3O_4$ composites in electrochemical lithium insertion and extraction is shown in Figure 4. The reversible capacity of MWNTs electrode is low, but it shows rather good stability toward electrochemical cycling. $Co_3O_4$ electrode has a better capacity, but the capacity fading is very severe and the stability toward electrochemical cycling is terrible. The deficiency was greatly improved by coating MWNTs with $Co_3O_4$ nanocrytals. All the MWNTs/$Co_3O_4$ composite electrodes have higher capacity than MWNTs, even the reversible capacities of C–$Co_3O_4$-10% and C–$Co_3O_4$-60% are higher than that of $Co_3O_4$ after three cycles. They all have better stability compared with $Co_3O_4$. The C–$Co_3O_4$-60% electrode preserves a better stability, keeping a high capacity, whose average fade rates is 0.47%/cycle, which is much lower than 6.04%/cycle of $Co_3O_4$. The fact that the $Co_3O_4$ particles homogeneously distribute on the surface of MWNTs and MWNTs can absorb the mechanical stress from the volume change in repetitive charging and discharging operations may be the reasons why the MWNTs/$Co_3O_4$ composite electrodes have better cycle-ability than pure $Co_3O_4$, and have higher reversible capacities than MWNTs.

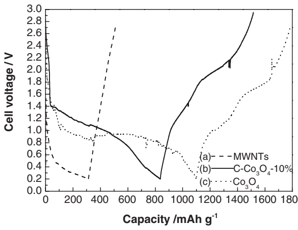

**Figure 3.** The voltage vs capacity plot of MWNTs (a), C–$Co_3O_4$-10% composite electrodes (b), and $Co_3O_4$ (c). Charge–discharge current density was 45 mA/g.

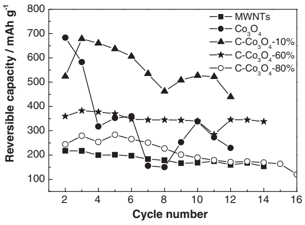

**Figure 4.** Cycle performance of the electrochemical lithium insertion and extraction for MWNTs, $Co_3O_4$ and MWNTs/$Co_3O_4$ composites.

In conclusion, a facile and effective method was introduced to in situ coat the MWNTs with thick layer of $Co_3O_4$ nanocrystals, whose sizes were less than 10 nm. The composites have larger lithium storage capacities and a better cycle-ability, and have potential application in Li-ion batteries.

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