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Octahedral Co₃O₄ particles threaded by carbon nanotube arrays as integrated structure anodes for lithium ion batteries[†]

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Octahedral Co_3O_4 particles threaded by ultra-long multi-walled carbon nanotube (MWCNT) arrays were prepared by a hydrothermal process and subsequent calcination. The Co_3O_4 octahedron with the (111) facets attaches to MWCNTs uniformly and closely. The composite can be used as an integrated anode for lithium ion batteries (LIBs) without any other additives (such as conductive additives and polymer binder), which exhibits a high reversible capacity of 725 mA h g⁻¹ at a current density of 100 mA g⁻¹, and excellent cyclic stability without capacity degradation over 100 cycles at a current density of 500 mA g⁻¹. The high performance can be attributed to the unique structure: (i) the ultra-long MWCNT array facilitates fast electron transfer; (ii) the tight adhesion between Co_3O_4 and MWCNTs prevents particle drifting and agglomeration; (iii) the free space between MWCNTs promotes fast ion transport and alleviates the large volume variation during discharge–charge process. This work demonstrates the great potential of MWCNT arrays as substrate and provides insights for the design and direct use of MWCNT array-based materials in LIBs, which will be helpful for future development of highperformance electrode materials.

1. Introduction

Lithium ion batteries (LIBs), as the dominant power sources for portable electronics and potential energy systems to drive electric vehicles, have attracted great attention in recent years.^{1,2} Graphite-based materials are the most commonly used anode materials in commercial LIBs but exhibit limited capacity and poor rate capability due to the intercalation reaction and low interlayer lithium diffusion coefficient.^{3–5} Therefore, further improvements to meet the demand of high energy and high power density require new materials and nanostructures with high capacity and good rate capability, as well as reduced weight of inactive components in the electrodes.³

 Co_3O_4 has been considered one of the promising candidates due to its low cost, chemical stability and high theoretical capacity (890 mA h g⁻¹) that is two times higher than that of the graphite (372 mA h g⁻¹).^{6,7} Despite the above advantages, the practical application of Co₃O₄ as anode for LIBs is hampered by the poor cycling performance and low rate capability, which is caused by its low electrical conductivity, easy agglomeration and large volume change during the conversion reaction processes.8 Although it remains a challenge to fabricate Co₃O₄ electrodes with high capacity and rate capability over extended cycling, various approaches have been attempted to improve its electrochemical performance. For example, dispersing the Co₃O₄ particles on various carbon substrates not only improves the electric conductivity, but also prevents the aggregation of active materials and cushions the drastic volume change.^{7,9-11} Design of unique nanostructured Co₃O₄ such as nanotubes,¹² nanowires,¹³ nanosheets,¹⁴ octahedral cages,¹⁵ peapod-like¹¹ and mesoporous¹⁶ structures is proposed as another effective method to improve the properties of Co3O4 electrodes. Recently, the research revealed that crystal facet structure is important for lithium transport and distinctly affects the electrochemical properties of electrode materials.^{17,18} Sun *et al.* reported that the (111) facets of Co_3O_4 have a more open surface structure than (100) and (110), which is beneficial for the diffusion of lithium ions and enables improved electrochemical performance.¹⁹ Li's group found that Co₃O₄ octahedra with (111) facets show higher reversible capacity and better rate capability compared to Co₃O₄ cubes with (001) facets and truncated octahedra with (001) and (111) facets.²⁰

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Paper

MWCNT arrays

Herein, we report facile hydrothermal process to fabricate high-performance LIB anodes constructed from uniform Co_3O_4 octahedra with (111) facets threaded by ultra-long multi-walled carbon nanotube (Co_3O_4 /MWCNT) arrays, as illustrated in Fig. 1. The loading amount of Co_3O_4 can reach as high as 94.5 wt% and be easily controlled by changing the content of the cobalt salt. The composite can be used directly as a selfsupported electrode without binders, conductive additives or metal current collectors. The high electronic conductivity of MWCNT array, abundant porosity between MWCNTs and the intimate contact between the Co_3O_4 and MWCNTs enable the composite to be a promising anode for high-performance LIBs.

2. Experimental

2.1. Sample preparation

Synthesis of the MWCNT arrays. The ultra-long vertically aligned MWCNT arrays were prepared by the floating catalyst chemical vapor deposition method using ferrocene as the catalyst precursor and cyclohexane as the solvent and carbon source.²¹

Synthesis of the Co3O4/MWCNT arrays. A hydrothermal method was used to synthesize the composites. Briefly, appropriate amounts of the MWCNT arrays, different amounts of Co(NO₃)₂. 6H₂O (1.45, 2.32 and 2.91 g for composites with Co₃O₄ contents of 59.9, 86.9 and 94.5 wt% according to thermogravimetric analysis (TGA); Fig. S1, ESI⁺), denoted as Co₃O₄/MWCNT40.1, Co₃O₄/ MWCNT13.1 and Co₃O₄/MWCNT5.5, respectively), hexadecyltrimethyl-ammonium bromide (CTAB, 10 mg), ethylene glycol (5 mL) and de-ionized water (50 mL) were mixed and mildly stirred for 6 h. The mixture was transferred and sealed in an 80 mL Teflon-lined stainless steel autoclave for a hydrothermal reaction at 160 °C for 18 h. After cooling to room temperature, the product was collected and washed with water and alcohol, and dried at 80 °C in air for 12 h. In order to increase the crystallinity of Co₃O₄, the samples were heated in air at 250 °C for 2 h and the Co₃O₄/MWCNT arrays were obtained.

Synthesis of the Co_3O_4 . Pure Co_3O_4 sample was synthesized under the same conditions as the composites but without adding MWCNT arrays.

2.2. Characterization

The morphology, composition and structure of the samples were characterized by transmission electron microscopy (TEM) (Tecnai F20, 200 kV), scanning electron microscopy (SEM) (FEI Nova NanoSEM 430, 15 kV), X-ray diffraction (XRD) (D-MAX/ 2400, Cu K) and TGA (Netzsch-STA 449C, measured from 30 to 800 °C at a heating rate of 10 °C min⁻¹ in air). The conductivities

of the MWCNTs and Co₃O₄/MWCNT composites were measured by a standard four-point probe resistivity measurement system (RTS-9, Guangzhou, China). Three measurements were taken at different positions on each sample, and then were averaged to get the final value.

2.3. Electrochemical measurements

The electrochemical properties of the Co₃O₄/MWCNT arrays. MWCNT arrays and Co_3O_4 as anode materials in LIBs were evaluated by a galvanostatic charge-discharge technique. The Co₃O₄/MWCNT arrays and MWCNT arrays were cut and used as integrated electrodes directly. The mass loading of the Co₃O₄/ MWCNT arrays and MWCNT arrays was 1-2 mg cm⁻² and the capacity was normalized on the total mass of the electrodes. The Co₃O₄ electrode was prepared by mixing 80 wt% active material with 10 wt% conductive carbon black (super P) as a conducting agent and 10 wt% polyvinylidene fluoride dissolved in N-methyl-2-pyrrolidone as a binder. Coin cells were assembled in an argon-filled glove box with the samples as test electrode, metallic lithium as the counter/reference electrode, a mixture of 1 M LiPF₆ in ethylene carbonate, dimethyl carbonate and ethylmethyl carbonate (1:1:1 vol) as the electrolyte, and Celgard 2400 polypropylene as the separator. Charge-discharge measurements were carried out galvanostatically at various current densities over a voltage range of 0.001 to 3 V (vs. Li/Li⁺) using a battery testing system (LAND CT2001A). After 100 cycles of discharge-charge, the cell was disassembled in the glove box, and the working electrode was taken out and washed three times using a dimethyl carbonate solution. It was then transferred to the vacuum chamber of the SEM and TEM for structure characterization. Cyclic voltammogram (CV) measurements were carried out using a VSP-300 multichannel potentiostat/galvanostat (Bio-Logic, France) workstation in the voltage range of 0.001-3.0 V (vs. Li⁺/Li) at a scan rate of 0.1 mV s⁻¹.

3. Results and discussion

Fig. 2a shows the SEM image and a photograph (inset of Fig. 2a) of the ultra-long MWCNT arrays with an average length of \sim 5 mm (Fig. S2, ESI[†]). The MWCNT arrays comprise numerous densely packed and aligned carbon nanotubes entangled together to form a porous configuration. The diameter distribution is between 10 and 60 nm (Fig. S3, ESI⁺). After hydrothermal reaction and subsequent calcinations, the appearance of the Co₃O₄/MWCNT13.1 composite (inset of Fig. 2b) is very similar to MWCNT arrays, while the weight increases significantly and each MWCNT is covered by octahedral Co3O4 particles over the entire length (Fig. 2b and c and Fig. S4, ESI[†]). The octahedral Co₃O₄ particles threaded by carbon nanotube arrays can be clearly seen in Fig. 2c (marked by the white and red arrows) and Fig. S5 (ESI⁺). The average size of the Co₃O₄ octahedron was \sim 455 nm in the long axis and \sim 360 nm in the short axis (Fig. S6, ESI⁺), which is quite different from Co_3O_4 without MWCNT arrays, showing an urchin-like structure in Fig. S7 (ESI⁺). The MWCNTs provide the nucleation sites for the crystal growth and the Co₃O₄ particles progressively grow to



Fig. 2 (a) SEM image and photograph (inset) of the ultra-long MWCNT arrays. (b, c) SEM images and digital photograph (inset of Fig. 2b) of the Co_3O_4 /MWCNT13.1 composite (the arrows in Fig. 2c show the threaded structure and the red arrows indicate the Co_3O_4 particles progressively growing to encircle the MWCNTs). (d) TEM image of the Co_3O_4 /MWCNT13.1 composite. (e) HRTEM image of the marked Co_3O_4 octahedra in (d), and (f) the corresponding SAED pattern of the octahedral Co_3O_4 particle.

encircle the MWCNTs (indicated by the red arrows, Fig. 2c). On the contrary, when there are no MWCNTs to provide nucleation sites for crystal growth, Co₃O₄ particles will form and spontaneously aggregate into large spheres to minimize the overall surface energy of the system.²² Subsequently, needle-like nanowires were grown on the surface assembling into an urchin-like structure, which can further minimize the surface energy.23 The TEM image further reveals that the MWCNTs pass through the octahedral particles which are encased by eight (111) facets (Fig. 2d). Even after strong ultrasonication in ethanol, they were still firmly strung around the MWCNTs indicating the tight adhesion. A high-resolution TEM (HRTEM) image clearly demonstrates the Co₃O₄ is well crystallized and the adjacent fringe spacing of 0.46 nm corresponds to the (111) facet of the Co_3O_4 structure (Fig. 2e). The corresponding selected area electron diffraction (SAED) pattern (Fig. 2f) of the particle shows a single-crystal spot pattern that can be indexed as Co₃O₄ as well.²⁴ The crystallographic structure of the samples was analyzed by XRD as shown in Fig. 3. The diffraction peak at around



Fig. 3 XRD patterns of the MWCNT arrays, Co₃O₄ and Co₃O₄/MWCNT composites.



Fig. 4 CVs of the (a) $Co_3O_4/MWCNT13.1$ composite and (b) Co_3O_4 at a scan rate of 0.1 mV s⁻¹ for five cycles.

 26° denoted by a pink rectangle originates from MWCNTs. All the other diffraction peaks can be indexed to Co_3O_4 (JCPDS No. 43-1003) and no other peaks of impurities are observed, indicating the high purity of the samples.

CV was carried out to understand the electrochemical reactive process of the samples in the range of 0.001-3.0 V for five cycles at a scan rate of 0.1 mV s^{-1} . One pair of redox peaks can be observed for Co₃O₄/MWCNT13.1 composite in Fig. 4a. The intense peak located at around 0.75 V in the first cathodic scan corresponds to the reduction of Co3O4 to metallic cobalt accompanying the formation of Li₂O and the solid electrolyte interphase (SEI) film.^{7,25} In the anodic process, a broad peak located at around 2.15 V can be ascribed to the reversible oxidation reaction from cobalt to Co₃O₄.²⁶ There are no distinguishable reduction and oxidation peaks for MWCNT due to the low amount and low electrical double layer capacitance of MWCNTs.²⁷ From the second cycle, the cathodic peak shifts to a higher potential of about 1.05 V while the oxidation peak position remains almost unchanged and the CV curves exhibit similar shapes, indicating good reversibility of lithium storage. In contrast, the Co3O4 electrode exhibits a pair of asymmetric redox peaks in the first cycle, and the cathodic peaks shift to lower potential suggesting sluggish lithium ion reaction kinetics (Fig. 4b). The intensity of the redox peaks from Co₃O₄ drops significantly and almost disappears after the second cycle, indicating the occurrence of irreversible reactions.

Fig. 5a shows galvanostatic charge-discharge voltage profiles of the MWCNT array, Co₃O₄ and Co₃O₄/MWCNT composite electrodes between 0.001 and 3.0 V at a current density of 100 mA g^{-1} . In the first discharge curve, an extended voltage plateau at around 1.0 V for the Co3O4 and Co3O4/MWCNT composites, which is ascribed to the reduction of Co₃O₄ to Co according to $\text{Co}_3\text{O}_4 + 8\text{Li}^+ + 8\text{e}^- \rightarrow 4\text{Li}_2\text{O} + 3\text{Co}^{12}$ A more inclined discharge slope between 1.0 V and the cutoff voltage is present for all the samples, which corresponds to the partial capacity contribution from the MWCNTs. In the charge curves, the sloped region from 1.5 to 2.2 V corresponds to the reversible oxidation of Co₃O₄, which is consistent with CV measurements. The Co₃O₄/MWCNT13.1 composite exhibits an initial reversible capacity of 725 mA h g^{-1} with a Coulombic efficiency of 76.3%, higher than those of Co_3O_4 /MWCNT5.5 composite (723 mA h g⁻¹, 71.1%), Co_3O_4 /MWCNT40.1 composite (512 mA h g⁻¹, 68.1%), MWCNT arrays (287 mA h g^{-1} , 59.8%) and Co₃O₄ (365 mA h g^{-1} , 33.9%) (Fig. 5a and b). The initial capacity loss can be mainly attributed to the irreversible processes such as electrolyte decomposition and the formation of a SEI film.^{7,28} In the subsequent cycling at 100 mA g^{-1} , the charge and discharge capacities of the Co₃O₄/MWCNT composites were kept well without any capacity loss after 40 cycles, suggesting excellent capacity retention of the Co₃O₄/MWCNT composite electrodes (Fig. 5b). However, the Co₃O₄ electrode displayed inferior cycling performance with a specific capacity of 110 mA h g⁻¹ after 40 cycles, showing a retention capacity of only 30.1%. The good electric conductivity provided by MWCNT and the open porosity between MWCNTs enabled easy ion accessibility, promoting the conversion reaction and improving the efficiency. The sufficient void space between MWCNTs and the flexible property of MWCNT can accommodate the volume change of Co₃O₄ during cycling, thus extending the cycling stability.

The rate capability of the MWCNT array, Co₃O₄ and Co₃O₄/ MWCNT composite electrodes were investigated as shown in Fig. 5c. The results show that the Co₃O₄/MWCNT13.1 composite exhibits the highest capacity above 720 mA h g⁻¹ compared to the other samples in the first 5 cycles at 100 mA g^{-1} . Upon increasing the current density, the capacities of the Co₃O₄/ MWCNT13.1 composite are better than MWCNT arrays, Co₃O₄ and the other two composites. The specific capacity of the Co_3O_4 /MWCNT13.1 composite still retains 450 mA h g⁻¹ at a high rate of 2500 mA g^{-1} . Notably, the result is comparable or even superior to recently reported state-of-art Co₃O₄-based anode materials, such as Co₃O₄/graphene composite showing capacities of ~450 mA h g^{-1} at 2000 mA g^{-1},^{29} grapheneanchored Co₃O₄ nanoparticle composite delivering capacities of ~480 mA h g⁻¹ at 500 mA g⁻¹,⁷ graphene-encapsulated mesoporous Co3O4 composite microspheres delivering capacities of ~264 mA h g⁻¹ at 2000 mA g⁻¹, ³⁰ Co₃O₄/carbon composite nanowires demonstrating capacities of ~ 358 mA h g⁻¹ at 800 mA g^{-1} ,²⁵ and peapod-like Co₃O₄/carbon nanocomposites exhibiting capacities of ~400 mA h g⁻¹ at 1000 mA g⁻¹.¹¹ Furthermore, when the current density is decreased from 2500 to 500 mA g^{-1} , the discharge capacity can be recovered (even a little higher than the original capacity at 500 mA g^{-1}), indicating



Fig. 5 (a) First galvanostatic charge–discharge curves of the $Co_3O_4/MWCNT$ composites, MWCNT arrays and Co_3O_4 at a current density of 100 mA g⁻¹. (b) Cycling performance and the first Coulombic efficiency of the $Co_3O_4/MWCNT$ composites, MWCNT arrays and Co_3O_4 at a current density of 100 mA g⁻¹ for 40 cycles. Solid symbols: discharge; hollow symbols: charge. (c) Rate capacity of the $Co_3O_4/MWCNT$ composites, MWCNT composites, MWCNT arrays and Co_3O_4 at different current densities. (d) Cyclic performance of the $Co_3O_4/MWCNT$ composites, MWCNT arrays and Co_3O_4 at a current density of 500 mA g⁻¹.

the electrode structure remains stable even under the high rate of cycling. The conductivities of the MWCNTs, Co₃O₄/ MWCNT40.1, Co₃O₄/MWCNT13.1 and Co₃O₄/MWCNT5.5 composites were 1390, 1064, 893 and 658 S m⁻¹ measured by a standard four-point probe configuration. The Co₃O₄/MWCNT5.5 composite electrode with the highest Co₃O₄ loading delivers lower capacity compared with Co3O4/MWCNT13.1 composite electrode probably due to inefficient electron transfer. Alternatively, the Co₃O₄/MWCNT40.1 composite electrode exhibits good rate performance with lower capacity because of insufficient active material loading. These results give hints that the suitable content of the conductive additive is ca. 10-15% and a higher amount does not contribute to the capacity or even degrades the performance in LIBs. The cyclic stability of the samples was investigated at a current density of 500 mA g^{-1} after cycling at 100 mA g^{-1} for two cycles, as shown in Fig. 5d. The Co₃O₄ electrode showed a significant capacity decrease from 423 to 130 mA h g^{-1} after only a few cycles. The large particle size with a long diffusion length for lithium ion transportation from the surface to the centre mean the central active materials cannot be fully accessed by the electrolyte leading to the inferior properties. In sharp contrast, the Co₃O₄/MWCNT composite electrodes showed a stable cycling performance with a Coulombic efficiency close to 100% from the second cycle during 100 cycles. A small increase in capacity with cycling can be attributed to the reversible growth of a polymeric gel-like film resulting from kinetically activated electrolyte degradation and electrochemical activation process.^{6,28,31-33} The high performance is attributed to the unique morphology and structural characteristics of the composites. The obtained Co₃O₄ octahedra with (111) facets is favorable for Li⁺ diffusion and Co₃O₄ redox reaction,²⁰ the threaded structure and open porosity provide good electric conductivity, fast electrolyte transport, efficient contact and strain accommodation, contributing to the improved reversible capacity, cyclic stability and rate capability.

To understand the electrochemical performance of the unique structured composite, the Co_3O_4 /MWCNT13.1 composite and Co_3O_4 electrodes after 100 cycles were taken out from the coin cells and the morphology variation observed by SEM and TEM. As shown in Fig. 6a and Fig. S8 (ESI[†]), no obvious change in the morphology can be observed for the Co_3O_4 /MWCNT13.1 composite, in which the Co_3O_4 particles were still

Fig. 6 SEM images of (a) the $Co_3O_4/MWCNT13.1$ composite and (b) Co_3O_4 after 100 discharge–charge cycles.

strung around the MWCNTs with almost the same size and shape, demonstrating the structural integrity of the composite upon electrochemical cycling. In contrast, cracks can be observed in the Co_3O_4 electrode, and the morphology of the urchin-like Co3O4 particles becomes unclear and seriously agglomerated with many small particles on the surface (Fig. 6b), indicating the structural evolution and aggregation of Co₃O₄ during cycling that leads to the fast capacity fading. The morphological stability of the composite can be ascribed to the threaded structure that tightly strings the MWCNTs and Co_3O_4 together, preventing the detachment and migration of Co₃O₄ particles from the MWCNTs. On the other hand, the space between the MWCNTs can effectively accommodate the strain of volume change and prevents the agglomeration and pulverization of Co₃O₄ particles during cycling, which contributes to the improved cyclic stability and rate capability.

4. Conclusion

 Co_3O_4 octahedra particles with (111) facets were threaded on MWCNTs through a hydrothermal process with subsequent calcination. The Co₃O₄/MWCNT composites can be directly used as integrated anode materials in LIBs without any additives. The good adhesion with high electrical conductivity and stability, and the large space with easy access for electrolyte and strain buffering, allow the composite to achieve high performance. Remarkably, the composite electrodes exhibit greatly improved electrochemical performance, such as enhanced reversible capacity of above 720 mA h g^{-1} at 100 mA g^{-1} excellent cyclic stability without capacity loss over 100 cycles and good rate performance with a capacity of 450 mA h g^{-1} at a high rate of 2500 mA g^{-1} . Combined with the facile and scalable synthesis strategy, the composite architectures could be extended to the other oxides and find applications in catalysis, sensors and energy storage devices.

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