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Abstract

Carbon composite products with different structures have been developed and used as anode for lithium-ion batteries due to the superior elasticity of carbon, which can keep the morphology integrity of the electrode materials in the process of the multiple cycles. Herein, a novel structure of nanosheets-in-nanotube Co₃O₄/carbon arrays is fabricated by the method of modified chemical vapor deposition (CVD). The carbon nanotube (CNT) layer acting as an outside coater can efficiently prevent the electrode from fragmentation and consequently ensure its shape integrity. The specific structure shows the ultra-stable cycle life (850 mAh g⁻¹ after 200 cycles at 0.5C) and high rate capability (694 mAh g⁻¹ at 2C). The favorable electrochemical properties are contributed to the combination of the wrapped elastic carbon and the enclosed Co₃O₄ nanosheets in the lithiation process, which is confirmed by an in situ transmission electron microscope.

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Abstract

Carbon composite products with different structures have been developed and used as anode for lithium-ion batteries due to the superior elasticity of carbon, which can keep the morphology integrity of the electrode materials in the process of the multiple cycles. Herein, a novel structure of nanosheets-in-nanotube Co₃O₄/carbon array is fabricated by the method of modified chemical vapor deposition. The carbon nanotube

1 layer acting as an outside coater can efficiently prevent the electrode from
2 fragmentation and consequently ensure its shape integrity. The specific structure shows
3 the ultra-stable cycle life (850 mAh g⁻¹ after 200 cycles at 0.5C) and high rate capability
4 (694 mAh g⁻¹ at 2C). The favorable electrochemical properties are contributed to the
5 combination of the wrapped elastic carbon and the enclosed Co₃O₄ nanosheets in the
6 lithiation process, which is confirmed by an *in situ* transmission electron microscope.

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1. Introduction

Lithium-ion batteries (LIBs) have been widely used in many aspects as one of most promising secondary batteries because of their environmental friendliness, fast charge/discharge ability, high power density and long cycle life [1-4]. As the most commercially applied anode materials, graphite belongs to the single-electron type with the maximum theoretical capacity of 372 mAh g⁻¹ (LiC₆). In order to meet the increasing demand of the energy storage devices, the multi-electrons-materials are believed as the next-generation anode candidates for LIBs. Among them, the conversion-mechanism-based ones including metal oxides [5-8] and metal sulfides [9,10] were believed to be promising ones, due to their high capacity (about 2-2.5 times higher than commercial graphite). However, these classes of materials suffered from huge volume changes during charging-discharging process, leading to the pulverization of the electrode and thus the severe capacity fading [11-14]. To solve such a problem, the carbon composite products with different structures were prepared by many researchers, because carbon exhibits the superior elasticity theoretically, which can keep the morphology integrity of the electrode materials in the process of the multiple cycles. For instance, Ding *et al.* have made uniform core-shell Co@C microspheres through the *in situ* transformation from Co₃O₄@phenolic [15]; Co₃O₄/Co@N-doped carbon nanotubes have been fabricated by Chen's group with improving cycling stability [16]; Deng *et al.* made three-dimensionally hierarchical Co₃O₄/Carbon composites with excellent electrochemical performances [17]. In despite of the big processes made in this area [18], there are few reports on the structure of an array consisted of two-dimensional nanosheets-in-carbon nanotubes. Theoretically, such a novel structure's stability towards Li⁺ storage is dramatically improved, and thus the electrochemical performance will be greatly promoted. Whereas, it is a great challenge

1 to synthesize this type of structure.

2 Herein, we fabricated such a new ideal structure of nanosheets-in-nanotube
3 Co_3O_4 /carbon arrays (NIN arrays) by utilizing a modified chemical vapor deposition
4 method. This structure exhibited much improved cycling stability when tested as
5 anodes in LIBs. We also used an *in situ* transmission electron microscopy (*in situ* TEM)
6 [19] to observe the lithiation process of as-designed anode in real time, suggesting that
7 the carbon layer acting as an outside coater could efficiently prevent the electrode from
8 fragmentation and consequently ensure the shape integrity of the electrode.
9 Furthermore, the unique array feature could enable a fast Li^+ transportation, and the
10 inner ultrathin Co_3O_4 nanosheets (NSs) are beneficial to improve the electrochemical
11 performance due to their specific two-dimensional structure [20,21]. Above-mentioned
12 structural characteristics of an NIN will make it show the superior cycling stability and
13 a high rate capability.

14 **2. Experimental Section**

15 **2.1 Synthesis of NIN arrays**

16 The structure of NIN arrays was fabricated by the following steps. Firstly, the method
17 of chemical vapor deposition (CVD) was used to synthesis carbon nanotube (CNT)
18 arrays. The specific operation was to put the anodic aluminium oxide (AAO) template
19 (with a thin layer of Cu on the one side which can prevent the structures from collapsing
20 after removing the templates) and liquid paraffin into the tube furnace and heat to 850°C
21 in argon flow (100 sccm) for 1 h, then cool the furnace to room temperature in argon
22 flow sequentially. Secondly, with a reaction ion etching system (L-451D-L, ANELVA),
23 the prepared AAO@carbon was plasma etched for 1 h (Ar buffer gas, 100 W, 5 Pa) to
24 eliminate the amorphous carbon layer which shaped by the chemical vapor deposition.
25 Thirdly, the acquired AAO@carbon and 0.1 mol $\text{Co}(\text{NO}_3)_2$ was added into the aqueous

alkali (PH=9), then the mixed solution was put into reaction kettle and heated to 170°C for 12 h. After reaction, with the operation of filtration as well as rinse by DI water and alcohol, the obtained solid-state material was dried in an oven at 350°C for 2 h under the atmosphere of nitrogen. Ultimately, the Co₃O₄ nanosheets (NSs) which presented as black powder were successfully grown in the interior surface of the CNTs. In the final step of the process, the sample of NIN arrays was put into 3 M NaOH solution for 1 h to dissolving the AAO template. After the thoroughly rinsing and drying procedure, the structure of nanosheets-in-nanotube Co₃O₄/carbon array was obtained.

2.2 Characterization

Scanning electron microscopy (SEM, Hitachi S-4800, operated at 10 kV), transmission electron microscopy (TEM, JEOL JEM-2100F, with an accelerating voltage of 300 kV), fast Fourier transform (FFT) and high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM, JEOL JEM-2100F) were used to characterize the morphology of the Co₃O₄/carbon array. X-ray diffraction (XRD, Philips X'Pert PRO MPD X-ray diffractometer, operated at 35 kV and 45 mA with Cu K α radiation) and energy dispersive spectrometer (EDS, JEOL JEM-2100F) element mapping were used to investigate the crystal phase, structure and chemical component of the samples. X-ray photoelectron spectroscopy (XPS) was used to characterize the element chemical states.

2.3 Electrochemical measurements

Three-electrode cells were used to measure the electrochemical properties of the NIN arrays and the Li metal foil was selected as the reference and counter electrode. There was 1 M LiClO₄ in ethyl carbonate (EC) and diethyl carbonate (DEC) (EC/DEC = 1/1 in v/v) which made up the electrolyte. Then the cells were assembled in a glove box which filled with pure argon gas. In a potential range of 3-0.05 V, the galvanostatic

discharge/charge measurements were performed vs Li^+/Li . The specific capacity of the NIN arrays was calculated based on the total weight of nanosheets-in-nanotube Co_3O_4 /carbon array.

2.4 Construction of the NIN-based LIBs

In situ transmission electron microscopy observations were implemented in a JEOL JEM-2100F equipped with a Nanofactory Instruments STM-TEM holder. In order to build up the test cell, an individual NIN was attached to the gold rod, which was further attached to the piezo-manipulator. A small piece of lithium foil was also attached to another gold wire as a reference and counter electrode. An ionic liquid electrolyte (ILE) was prepared in advance by dispersion of lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) into N-methyl-N-propylpiperidinium bis(trifluoromethanesulfonyl)imide (PP13TFSI). Before insertion of the holder into the TEM, a drop of the ILE was placed on the surface of metal lithium tip. It was easy to choose an isolated NIN. The lithiation was carried out at a negative bias in the range of -3-0 V with respect to the Li metal.

3. Results and discussion

Fig. 1. (a) Schematic design and fabrication process of nanosheets-in-nanotube Co_3O_4 /carbon arrays structure. (b) Schematic of the synthesis process of CNTs using the AAO template.

1 The synthetic procedure of the NIN arrays including three steps is shown in Fig. 1a.
2 Firstly, the carbon nanotubes (CNTs) were grown into the anodic aluminium oxide
3 (AAO) template. Herein, a modified CVD approach is used. As depicted by Fig. 1b, the
4 AAO template was put into a specially made small quartz tube vertically in the middle
5 of tube furnace and a porcelain boat loaded the C_4H_{10} was placed at the gas intake side
6 of the tube. The high temperature of 850°C can guarantee the C_4H_{10} transformation into
7 carbon on surface of the AAO template. In consideration of the large surface area and
8 well-distributed nanopores (Fig. S1a and S1b), AAO membranes have been widely
9 applied to synthesize nanomaterials in the energy field [22]. The panorama of the AAO
10 template presents its height of $\sim 60\text{ }\mu\text{m}$ (Fig. S1c) and its cross-section show a smooth
11 interior structure with the width of 200-400 nm (Fig. S1d). Secondly, Co_3O_4 NSs were
12 planted into inner-walls of CNTs with the assistant of an *in situ* growth method (Fig.
13 1a). In this step, the existence of AAO@CNTs is of key importance to ensure totally
14 forming Co_3O_4 NSs in CNTs instead of the outside walls of CNTs. It is worthy to note
15 that the presence of the trace of oxygen in CNTs will be beneficial to fabricate Co_3O_4
16 NSs due to their hydrophilic surfaces. Therefore, the Co_3O_4 NSs was planted inside the
17 CNTs. Finally, the designed nanosheets-in-nanotube Co_3O_4 /carbon array (NIN arrays)
18 structure was successfully obtained after removing the AAO template. As shown in Fig.
19 2a, the special structure of nanosheets-in-nanotube can be clearly observed by the
20 vertical section view of the NIN arrays.

Fig. 2. (a) SEM image on the cross section of the broken nanosheets-in-nanotube Co₃O₄/carbon arrays structure. (b) HRTEM image of Co₃O₄ nanosheets from a side view.

The detailed structure and morphology of NIN arrays and the pure CNTs were investigated, proving that the as-designed structure has been fabricated successfully. The X-ray diffraction (XRD) pattern of NIN arrays is shown in Fig. 3a, the peaks in pattern can be indexed to the spinel Co₃O₄ (JCPDS no. 42-1467) which authenticates the existence of Co₃O₄. According to the SEM image in Fig. 3b, the configuration of nanotube arrays can be observed arranging in order on the copper film and the length of the CNTs is ~50 μm. TEM image at higher magnification (Fig. 3c) of an individual carbon nanotube clearly reveals the morphology of the fabricated structure: nanosheets-in-nanotube, confirming to the schematic depicted as the inset in Fig. 3c. As can be seen, the width of a single tube is ~200 nm, the thickness of CNTs is ~10 nm and the thickness of Co₃O₄ NSs is 2-3 nm (Fig. 2b). The high-resolution TEM image of Co₃O₄ NSs shown in Fig. 3d exhibits the lattice fringes for an interplanar spacing of 0.47 nm, corresponding to the (111) lattice exposed facet of Co₃O₄. The presented (111) facet is usually considered as a high-energy facet relatively, which can bring about more active sites for Li⁺ storage, thus improving the electrochemical performance of the Lithium ion batteries [23]. The thermogravimetric curve of NIN arrays (Fig. S2) shows that a

weight loss of ~10% occurs in the temperature range from 300°C to 375 °C due to the loss of CNTs, which proves that the mass content of CNTs is ~10%.

Fig. 3. (a) XRD pattern of nanosheets-in-nanotube Co_3O_4 /carbon arrays on the Cu foil. (b) SEM characterizations of nanosheets-in-nanotube Co_3O_4 /carbon arrays. (c) TEM image at higher magnification of an individual nanosheets-in-nanotube Co_3O_4 /carbon array structure. Inset showing the schematic drawing of nanosheets-in-nanotube Co_3O_4 /carbon array. (d) HRTEM images of a nanosheets-in-nanotube Co_3O_4 /carbon array layer.

As a comparison, the pure CNTs were also made by the similar synthetic method (Fig. 4a). According to the XRD pattern in Fig. 4b, it is noted that there is a broad peak at about 22° which can be attributed to CNTs. Compared with the sharp peak of the pure CNTs, the contrasting result illustrates that the as-prepared sample is composed of both Co_3O_4 and carbon. SEM images of CNTs shows the structure of hollow tubes (Fig.

1 4c and 4d) with the size of ~ 200 nm wide and ~ 50 μm long which is accord with the
2 size of NINs. The most remarkable feature of NIN arrays is growing the Co_3O_4 NSs in
3 the interior wall of CNTs. The high-angle annular dark-field scanning transmission
4 electron microscopy (HAADF STEM) and energy dispersive spectrometer (EDS)
5 element mapping images of an NIN are also given as the direct evidence in Fig. 4.
6 Compared with the image of pure CNTs (Fig. 4e) the image of NIN array (Fig. 4f)
7 shows that the CNT is stuffed with Co_3O_4 NSs with smooth outer surface. It also can
8 be obviously observed that signals of oxygen and cobalt are uniformly covered within
9 the boundary (Fig. 4g and 4h), indicating that Co_3O_4 NSs are well introduced into CNTs.
10 Meanwhile, the carbon signals (Fig. 4j) are distributed wider than oxygen and cobalt
11 crossing the boundary, which means that the Co_3O_4 NSs are wrapped by CNTs
12 completely. It is noted that there are only signals of carbon and a very small amount of
13 oxygen in pure CNTs (Fig. 4e). It turns out to be the case that the Co_3O_4 NSs was
14 completely planted inside the CNTs.

1

2 Fig. 4. (a) Schematic of the fabrication process of the pure carbon nanotubes. (b) XRD
 3 pattern of carbon nanotubes. (c, d) SEM characterizations of carbon nanotubes. (e)
 4 HAADF STEM image and the EDS element mappings of C and O of carbon nanotubes.
 5 (f) HAADF STEM image of the nanosheets-in-nanotube Co_3O_4 /carbon arrays structure.
 6 The EDS element mappings of O (g), Co (h) and C (j) of the nanosheets-in-nanotube

Co₃O₄/carbon arrays structure.

Chemical states of cobalt states of the NIN arrays were carried out by XPS (Fig. 5).

The spectra of NIN arrays exhibit two peaks at 778.8 eV and 795.7 eV while two satellite peaks at 783.9 eV and 801.4 eV, corresponding to the Co 2p_{3/2} and Co 2p_{1/2} spin-orbit peaks of Co₃O₄ respectively, which is identical with the foregoing analysis testifying the formation of Co₃O₄ phase. According all these characterizations above, the unique structure of nanosheets-in-nanotube can be generally verified.

Fig. 5. High-resolution XPS spectra of nanosheets-in-nanotube Co₃O₄/carbon arrays.

The battery performance of NIN arrays was evaluated and compared with the commercial Co₃O₄ samples by galvanostatic charge/discharge measurement and electrochemical impedance spectroscopy (EIS) and the results are given in Fig. 6. Such NIN arrays indeed showed a superior and stable electrochemical performance. Fig. 6a shows the first galvanostatic charge/discharge cycle of NIN arrays under the current density of 0.2C (1C = 890 mAh g⁻¹). The potential plateau at 1.2 V is related to the conversion of Co₃O₄ into an intermediate phase CoO (or Li_xCo₃O₄), and then the metallic Co was formed, indicating a typical charge/discharge behavior of the Co₃O₄

1 electrode materials [24,25]. The initial charge and discharge capacities are 1189.3 mAh
2 g^{-1} and 1279.2 mAh g^{-1} , respectively. It is noted that there is a relatively high initial
3 Coulombic efficiency of 92.9%. The irreversible capacity loss in first cycle may be
4 caused by the irreversible reactions, electrolyte decomposition and the formation of SEI
5 layer on the surface of electrode [20]. In Fig. 6b, the comparative cyclic performances
6 of the NIN arrays and the commercial Co_3O_4 samples at a current density of 0.5C are
7 exhibited. The NIN array delivers a specific capacity of 850 mAh g^{-1} after 205 cycles
8 with a Coulombic efficiency of 99.9%, exhibiting a superior cycling performance and
9 good reversibility, while the capacity of commercial Co_3O_4 samples substantially
10 decreases to only 157 mAh g^{-1} after 50 cycles. The magnified Coulombic efficiency
11 curve (Fig. S3) also shows the fluctuation, which is consistent with variation trend of
12 the charge-discharge capacities. As demonstrated in Fig. 6c, rate capability of NIN
13 arrays is evaluated at different current densities ranging from 0.2C to 2C. As is revealed,
14 even at a high current density of 2C, the reversible capacity still remained around 694
15 mAh g^{-1} , which is 1.87 times higher than that of graphite (372 mAh g^{-1}). It demonstrates
16 that such special structure could facilitate Li^+ ion transportation. In addition, the
17 contrastive electrode kinetics of NIN arrays and commercial Co_3O_4 samples were
18 analyzed by EIS in Fig. 6d, which conducted with 5 mV amplitude in the frequency
19 range from 0.01 Hz to 100 kHz. On the high frequency region of the curves, the arc
20 diameter of NIN arrays is smaller than that of commercial Co_3O_4 , which means the
21 charge transfer resistance of NIN arrays is lower. In intermediate frequency region, the
22 included angle of spectral line and real axis of NIN arrays is close to 90° while the angle
23 of commercial Co_3O_4 is about 45° . The high angle indicating that the diffusion velocity
24 of ions to electrode is much faster. The diagonal in low frequency region is attributed
25 to the Warburg impedance of ions on the electrode. The higher slope of NIN arrays

1 explains that it has a higher electrochemical capacity than that of the commercial Co_3O_4 .
 2 Compared with the previously reported Co_3O_4 related anode materials for LIBs (Table
 3 1), NIN anode exhibited relatively enhanced electrochemical performances, especially
 4 on the aspect of cycle life. The desirable properties of NIN arrays are attributed to its
 5 unique nanosheets-in-nanotube structure features.

6
 7 Fig. 6. Electrochemical lithium storage properties of nanosheets-in-nanotube
 8 Co_3O_4 /carbon arrays: (a) Charge/discharge voltage profiles of nanosheets-in-nanotube
 9 Co_3O_4 /carbon arrays at a current density of 0.2C. (b) Cycling performance and
 10 Coulombic efficiency of nanosheets-in-nanotube Co_3O_4 /carbon arrays and commercial
 11 Co_3O_4 at a current density of 0.2C. (c) Rate performance of nanosheets-in-nanotube
 12 Co_3O_4 /carbon arrays at different current density. (d) EIS of nanosheets-in-nanotube
 13 Co_3O_4 /carbon arrays and commercial Co_3O_4 .

14 Table 1 Comparisons on LIBs performance between different Co_3O_4 -based anodes.

Electrode materials	First discharge-charge capacity (mAh g ⁻¹)	Cycling performance (mAh g ⁻¹)	Ref.
Co ₃ O ₄ NSs-in-CNT arrays	1279-1189 at 178 mA g ⁻¹	850 after 205 cycles at 445 mA g ⁻¹	This work
Peapod-like Co ₃ O ₄ @carbon nanotube	~1250~780 at 100 mA g ⁻¹	700 after 100 cycles at 100 mA g ⁻¹	[26]
Porous MWCNTs/Co ₃ O ₄ nanocomposites	1171-812 at 100 mA g ⁻¹	813 after 100 cycles at 100 mA g ⁻¹	[27]
Hollow-structured Co ₃ O ₄ particles	1107~800 at 50 mA g ⁻¹	880 after 50 cycles at 50 mA g ⁻¹	[28]
Co ₃ O ₄ /N-doped porous carbon	1730-1321 at 100 mA g ⁻¹	892 after 100 cycles at 100 mA g ⁻¹	[29]
Co ₃ O ₄ @a-TiO ₂ core-shell microcubes	1100-790 at 500 mA g ⁻¹	800 after 60 cycles at 500 mA g ⁻¹	[30]
Mesoporous nanostructured Co ₃ O ₄	1286-880 at 200 mA g ⁻¹	913 after 60 cycles at 200 mA g ⁻¹	[31]
Co/Co ₃ O ₄ -C ternary core-branch arrays	1195-880 at 445 mA g ⁻¹	608 after 200 cycles at 445 mA g ⁻¹	[32]
Co ₃ O ₄ /MWNT composites	960-670 at 100 mA g ⁻¹	708 after 100 cycles at 100 mA g ⁻¹	[33]
Self-stacked Co ₃ O ₄ nanosheets	1644~1050 at 178 mA g ⁻¹	1070 after 50 cycles at 178 mA g ⁻¹	[34]
Double-shelled Co ₃ O ₄ hollow spheres	1013~750 at 178 mA g ⁻¹	866 after 50 cycles at 178 mA g ⁻¹	[35]

1 The lithiation process of NIN array and its related storage mechanisms at the atomic
 2 level were unmasked via an *in situ* TEM [36]. An *in situ* battery prototype (the
 3 experimental part, ESI) was set up as illustrated in Fig. 7a. The structure is composed
 4 of a piece of NIN arrays, an ionic liquid electrolyte and a tablet of metallic Li. With a
 5 potential of -3 V between the metal Li electrode and NIN, the process of lithiation is
 6 brought to pass. The top-left inset in Fig. 7c is the fast Fourier transform (FFT) image
 7 that indicates the phase generation of Li₂O and Co. Upon lithiation (Fig. 7b and 7c),
 8 NIN was slightly expanded. In order to facilitate a detailed observation of the volume
 9 change of NIN, the area framed up by red squares in Fig. 7b and Fig. 7c are magnified
 10 and shown in Fig. 7d and Fig. 7e. Although the relatively high amounts of Co₃O₄ NSs
 11 were filled into CNTs, there still exist some void spaces in the hollow shell of CNT
 12 including the interspaces came from the room sites (areas circled by the red line in Fig.

7d and 7e) and the interval void spaces resulting from the crisscross of Co₃O₄ NSs (Fig. S1a). Therefore, when the intercalation of Li⁺ into Co₃O₄ NSs happens, these two kinds of hollow spaces can effectively buffer the volume expansion. Such a process is obviously visualized via an *in situ* TEM, as shown in Fig. 7d and 7e, after full lithiation, the void spaces still exist (Fig. 7e), which indicates that the elastic of CNT can effectively endure the expansion. Many theoretical studies at early time showed that the maximum elastic strain (fracture strain) of CNTs is about 18% [37-39], and the elastic strain of CNTs in this work is smaller by calculation (in Fig. 7d and Fig. 7e the diameter of CNTs increases from 200 nm to 210 nm; the formula of elastic strain is $\Delta d/d$), thus the whole structure will not be broken with the volume expansion. In addition, the volume expansion rate is 105% (200 nm to 210 nm) in the Li⁺-insertion process, much smaller than that of the pure Co₃O₄. These findings demonstrate that the ultrahigh elastic property of CNT and the unique structure features can strength the structural stability of NIN. The phase and structure evolution of a single Co₃O₄ nanosheet was further observed. Before Li⁺ intercalation, a nanosheet was a single crystal plate with a 0.47 nm lattice spacing (Fig. 7f), corresponding to (111) plane of Co₃O₄. After Li⁺ intercalation, the Co₃O₄ NSs turned to the confused particles and their main composition was further proofed as the metal cobalt (Fig. 7g) (0.21 nm interplanar spacing is assigned to (100) facet of cobalt). It also agrees with the transformation process in the classic conversion mechanism: Co₃O₄+Li⁺→Li₂O+Co. Above all, the whole NIN structure is well preserved during Li⁺ insertion, thus leading to superior cycling stability.

Fig. 7. (a) Schematic illustration of a LIB device with the anode of nanosheets-in-nanotube Co_3O_4 /carbon arrays under *in situ* TEM. (b, c) *In situ* TEM patterns during Li ion intercalation and the FFT patterns of a nanosheets-in-nanotube Co_3O_4 /carbon array. (d, e) TEM image at higher magnification of a nanosheets-in-nanotube Co_3O_4 /carbon array. (f, g) HRTEM images of a nanosheets-in-nanotube Co_3O_4 /carbon array layer before and after the Li ion intercalation. Inset showing the schematic drawing of the atomic structure.

The superior electrochemical performance of the stable structure of NIN arrays is considered to be attributed to its unique configuration. As shown in Fig. 8a, the outer

1 carbon layer can reinforce the whole structure as well as provide continuous conductive
2 paths. It can protect the interior Co_3O_4 NSs from wastage during the volume expansion
3 caused by the phase transition, promoting the cyclic performance and specific
4 capacities of the architecture. Besides, the interspaces in this array structure can be
5 easily filled with the electrolyte, which can enlarge the contacting area and enhance the
6 Li^+ transport. Just as significant, the crystal plane of Co_3O_4 also plays an important role
7 on its electrochemical performances. In our case, the (111) facets are highly exposed.
8 Relatively, the (111) facets have more cobalt atoms on the surfaces of Co_3O_4 crystals
9 which is 1.875 Co^{2+} (Fig. 8b) while the (001) facets have 1 Co^{2+} (Fig. 8c). From this
10 point of view, NIN arrays with highly exposed (111) facets is good for improving their
11 capacity of the structure. After cycling, the structure of nanotube is well preserved (Fig.
12 S4a), indicating the stability of NIN arrays. The XRD pattern (Fig. S4b) exhibits a broad
13 Co peak, suggesting the existence of ultra-small Co nanoparticles dispersed in Li_2O .

Fig. 8. (a) Schematic illustration of the Li ion insertion-extraction process for nanosheets-in-nanotube Co_3O_4 /carbon arrays. (b) A theoretical model of 3D and 2D surface atomic configurations in the (111) plane of Co_3O_4 . (c) A theoretical model of 3D and 2D surface atomic configurations in the (001) plane of Co_3O_4 .

4. Conclusions

In summary, a new structure, nanosheets-in-nanotube Co_3O_4 /carbon array, has been

1 successfully fabricated via a modified chemical vapor deposition method. As tested as
2 anode materials for LIBs, as-prepared NIN structure showed the superior
3 electrochemical performances, including excellent cycling life (850 mAh g⁻¹ after 200
4 cycles at 0.5C) and rate performance (694 mAh g⁻¹ at 2C). The real-time lithiation
5 process and the atomic storage mechanisms of an NIN were further investigated by
6 using an *in situ* TEM. During Li⁺-uptake, a NIN structure could exhibit a good structural
7 stability, resulting in its performance improvement.

8
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- 15

1 **Figure captions**

2 Fig. 1. (a) Schematic design and fabrication process of nanosheets-in-nanotube
3 Co_3O_4 /carbon arrays structure. (b) Schematic of the synthesis process of CNTs using
4 the AAO template.

5 Fig. 2. (a) SEM image on the cross section of the broken nanosheets-in-nanotube
6 Co_3O_4 /carbon arrays structure. (b) HRTEM image of Co_3O_4 nanosheets from a side
7 view.

8 Fig. 3. (a) XRD pattern of nanosheets-in-nanotube Co_3O_4 /carbon arrays on the Cu foil.
9 (b) SEM characterizations of nanosheets-in-nanotube Co_3O_4 /carbon arrays. (c) TEM
10 image at higher magnification of an individual nanosheets-in-nanotube Co_3O_4 /carbon
11 array structure. Inset showing the schematic drawing of nanosheets-in-nanotube
12 Co_3O_4 /carbon array. (d) HRTEM images of a nanosheets-in-nanotube Co_3O_4 /carbon
13 array layer.

14 Fig. 4. (a) Schematic of the fabrication process of the pure carbon nanotubes. (b) XRD
15 pattern of carbon nanotubes. (c, d) SEM characterizations of carbon nanotubes. (e)
16 HAADF STEM image and the EDS element mappings of C and O of carbon nanotubes.
17 (f) HAADF STEM image of the nanosheets-in-nanotube Co_3O_4 /carbon arrays structure.
18 The EDS element mappings of O (g), Co (h) and C (j) of the nanosheets-in-nanotube
19 Co_3O_4 /carbon arrays structure.

20 Fig. 5. High-resolution XPS spectra of nanosheets-in-nanotube Co_3O_4 /carbon arrays.

21 Fig. 6. Electrochemical lithium storage properties of nanosheets-in-nanotube
22 Co_3O_4 /carbon arrays: (a) Charge/discharge voltage profiles of nanosheets-in-nanotube
23 Co_3O_4 /carbon arrays at a current density of 0.2C. (b) Cycling performance and
24 Coulombic efficiency of nanosheets-in-nanotube Co_3O_4 /carbon arrays and commercial

1 Co_3O_4 at a current density of 0.2C. (c) Rate performance of nanosheets-in-nanotube
2 Co_3O_4 /carbon arrays at different current density. (d) EIS of nanosheets-in-nanotube
3 Co_3O_4 /carbon arrays and commercial Co_3O_4 .

4 Fig. 7. (a) Schematic illustration of a LIB device with the anode of nanosheets-in-
5 nanotube Co_3O_4 /carbon arrays under *in situ* TEM. (b, c) *In situ* TEM patterns during Li
6 ion intercalation and the FFT patterns of a nanosheets-in-nanotube Co_3O_4 /carbon array.
7 (d, e) TEM image at higher magnification of a nanosheets-in-nanotube Co_3O_4 /carbon
8 array. (f, g) HRTEM images of a nanosheets-in-nanotube Co_3O_4 /carbon array layer
9 before and after the Li ion intercalation. Inset showing the schematic drawing of the
10 atomic structure.

11 Fig. 8. (a) Schematic illustration of the Li ion insertion-extraction process for
12 nanosheets-in-nanotube Co_3O_4 /carbon arrays. (b) A theoretical model of 3D and 2D
13 surface atomic configurations in the (111) plane of Co_3O_4 . (c) A theoretical model of
14 3D and 2D surface atomic configurations in the (001) plane of Co_3O_4 .