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J. Wang, H. L. Xin

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High-rate and long-life lithium-ion battery performance of hierarchically hollow-structured NiCo$_2$O$_4$/CNT nanocomposite

Jie Wang$^{a,1}$, Jianzhong Wu$^{a,1}$, Zexing Wu$^{c}$, Lili Han$^{a}$, Ting Huang$^{a}$, Huolin L. Xin$^{b}$, and Deli Wang$^{a,*}$

$^a$ Key laboratory of Material Chemistry for Energy Conversion and Storage (Huazhong University of Science and Technology), Ministry of Education, Hubei Key Laboratory of Material Chemistry and Service Failure, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, PR China

$^b$ Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY 11973, USA

$^c$ School of Materials Science and Engineering, Tianjin University, Tianjin 300072, PR China

Abstract

3D-transition binary metal oxides have been considered as promising anode materials for lithium-ion batteries with improved reversible capacity, structural stability and electronic conductivity compared with single metal oxides. Here, carbon nanotube supported NiCo$_2$O$_4$ nanoparticles (NiCo$_2$O$_4$/CNT) with 3D hierarchical hollow structure are fabricated via a simple one-pot method. The NiCo$_2$O$_4$ nanoparticles with interconnected pores are consists of small nanocrystals. When used as anode material for the lithium-ion battery, NiCo$_2$O$_4$/CNT exhibits enhanced electrochemical performance than that of Co$_3$O$_4$/CNT and NiO/CNT. Moreover, ultra-high discharge/charge stability was obtained for 4000 cycles at a current density of 5 A g$^{-1}$. The superior battery performance of NiCo$_2$O$_4$ nanoparticles is probably attributed to the special structural features and physical characteristics, including integrity, hollow structure with interconnected pores, which providing sufficient accommodation for the volume change during charge/discharge process. Besides, the consisting of ultra-small crystals enhanced the utility of active material, and intimate interaction with CNTs improved the electron-transfer rate.

Keywords: NiCo$_2$O$_4$ nanoparticles; Hierarchical hollow structure; interconnected pores; lithium storage; long-life stability
1. Introduction

Lithium ion batteries (LIBs) are regarded as one of the most promising renewable energy storage devices owing to their widely application in electric vehicles, portable devices and renewable energy integration. In the past years, the increasing demands for high-rate and long cycle life lithium ion batteries has stimulated the investigation of high theoretical capacity electrode materials[1], especially metal oxides (e.g. Co$_3$O$_4$[2, 3], MnO$_2$[4, 5], Fe$_3$O$_4$[6, 7], Fe$_2$O$_3$[8-10], SnO$_2$[11, 12], TiO$_2$[13, 14]), of which the theoretical capacity are larger than 700 mA h g$^{-1}$, much higher than graphite carbon (372 mA h g$^{-1}$). However, transition metal oxide anode materials with bulk structure are susceptible to cause large volume change during lithiation/delithiation and the low lithium diffusivity, which would lead to structure pulverization, even resulting in poor cycling stability and rate capability[15, 16]. Therefore, the investigation of transition metal oxide materials with different morphologies at micro- to nanoscales is noted to be one of the substantive solutions for the accommodation of volume change to some extent, which is attributed to their higher surface-to-volume ratio and short path length for Li-ion diffusion. Comparative study for recent references revealed that excellent battery performance for metal oxides with different nanostructure. Mesoporous peapod-like Co$_3$O$_4$@carbon nanotube arrays has been reported as anode electrode material via a controllable nano-casting process, in which Co$_3$O$_4$ nanoparticles are confined exclusively in the intra tubular pores of the nanotube arrays[17]. The open pores between nanotubes render the Co$_3$O$_4$ nanoparticles accessible for effective electrolyte diffusion. As a result, such architecture exhibited excellent rate capacity, cycling performance as well as high specific capacity. One-dimensional (1-D) hierarchical NiO nanosheets covering bamboo-like amorphous CNT composites (NiO@CNT) were synthesized by using sulfonated polymeric nanotubes (PNTs) as both a template and a source of nano-structured carbon derived by low-temperature thermal carbonization treatment[18]. As an anode material, this hybrid material exhibited excellent electrochemical performance owing to the synergistic effects of the hollow amorphous CNT backbone and ultrathin NiO nanosheets.

Recently, binary transition metal oxides with controllable nanostructure such as Co$_x$Mn$_{3-x}$O$_4$[19, 20], Co$_x$Fe$_{3-x}$O$_4$[21, 22], Co$_3$V$_2$O$_8$[23, 24], NiCo$_2$O$_4$[25-27] et al have been reported in order to acquire the advantages of physical or electrochemical characteristics for two or more kinds of transition metal oxides. Among various binary metal oxides, NiCo$_2$O$_4$ is considered as a promising electrode material, in which one Co atom is replaced by Ni,
possessing much better electrical conductivity and higher electrochemical activity than nickel oxides or cobalt oxides [28, 29]. In addition, hollow structure with porous architecture could not only shorten the pathways for Li ion diffusion owing to the adequate interface contact between electrode and electrolyte, but also enlarge the surface area which is benefit to accommodate the volume change during the charge/discharge processes [30, 31]. In general, hollow structured materials are synthesized by template- or surfactants- directed methods [32-34] which is time consuming and costly, so far, a large scale production of hollow structured materials without using template- or surfactants is appealing via the widespread usage of low-cost raw transition metal materials.

Herein, a simple strategy for the synthesis of multi-walled carbon nanotubes supported three dimensional hierarchical hollow structured NiCo$_2$O$_4$ binary nanocomposites (NiCo$_2$O$_4$/CNT) is developed. The formation of hollow structure is based on the Kirkendall effect [35], in which no template or surfactant is needed. The hollow shell, composed of small nanocrystals, leave small interspaces for accommodating volume change during lithiation/delithiation and making full contact between electrolyte and active materials. When evaluated as anode materials for LIBs, the Li$^+$ ions can diffuse into the NiCo$_2$O$_4$ hollow structure through these pores within short distance and small resistance, favorably enhancing the electrochemical behaviors. It has been found that the NiCo$_2$O$_4$/CNT composite with hierarchical hollow structure, interconnected pores and high electronic conductivity, delivered a high reversible capacity of 892 mA h g$^{-1}$ at a current density of 1 A g$^{-1}$ even after 200 charge/discharge cycles and still retained the hollow morphology, indicating its good potential application for high power applications in LIBs. Moreover, the NiCo$_2$O$_4$/CNT also showed high reversible capacity of 500 mA h g$^{-1}$ even after 4000 cycling with the average Coulombic efficiency above 99%, confirming the excellent high-rate stability.

2. Experimental part
2.1. Materials synthesis

The synthesis of NiCo$_2$O$_4$/CNT was based on the simple impregnation-reduction-oxidation method. In detail, 0.90 mmol of CoCl$_2$·6H$_2$O, 0.45 mmol of NiCl$_2$·6H$_2$O and 10 mmol of MWCNTs were added into a 25 mL baker, then 10 mL purified water was poured into the baker followed by magnetic stirring at 60 °C along with ultrasonic dispersion until the solution evaporated to form a thick slurry. The composite was then transferred into a vacuum drying oven at 40 °C overnight. After milled in agate mortar[36], the resulting powder was annealed at 400
°C for 3 h under flowing Ar/H<sub>2</sub> atmosphere. In the end, the binary metallic composites were calcined in air condition at 350 °C for 10 hours.

The synthesis of hollow structured Co<sub>3</sub>O<sub>4</sub>/CNT and NiO/CNT nanoparticles was conducted via the same approach. The synthesis of hollow structured NiCo<sub>2</sub>O<sub>4</sub> nanoparticles was conducted via the same approach, but the oxidation temperature was changed to 500 °C.

2.2. Material Characterization

Powder X-ray diffraction (XRD) was performed by using an X'Pert PRO diffractometer, and diffraction patterns were collected at a scanning rate of 4 ° min<sup>-1</sup>. Thermal gravimetric analysis (TGA) was conducted on TA-Q500 Instrument at a heating rate of 10 °C min<sup>-1</sup>. SEM images were obtained by using Nova NanoSEM 450. X-ray fluorescence (XRF) results were obtained via EAGLE III. ADF-STEM/TEM images were obtained using 200 and 300 keV field-emission S/TEMs. Electron Energy Loss Spectroscopy (EELS) data were acquired using a Gatan Tridiem spectrometer.

2.3. Electrochemical Measurements

For the electrochemical measurements, the working electrode was consisted of active material, electrical conductor (carbon black) and PVDF (in a weight ratio of 8: 1: 1) on a copper foil. For lithium-ion batteries, pure lithium foil was used as the counter electrode and a 1.0 M LiPF<sub>6</sub> in 1:1 v/v ethylene carbonate (EC)/dimethyl carbonate (DMC) as the electrolyte. The 2032 coin cells were assembled in an Ar-filled glovebox. Galvanostatic cycling results were obtained by using a Neware battery test system from 0.05 to 3.0 V. Cyclic voltammetry (CV) measurements were tested using a CHI 1040 with a potential range from 0.01 to 3.0 V.

3. Results and discussion

The hollow structured NiCo<sub>2</sub>O<sub>4</sub>/CNT nanoparticles with three dimensional interconnected pores were obtained via a simple two-step method. NiCo<sub>2</sub>/CNT alloy composite was first formed by using an impregnation reduction method [37, 38], where the homogeneous mixture of NiCl<sub>2</sub>, CoCl<sub>2</sub>, and MWCNTs slurry was reduced under Ar/H<sub>2</sub> atmosphere at 400 °C for 3 h. The NiCo<sub>2</sub> alloy particles with smooth surface are uniformly distributed on multi-
walled carbon nanotubes (MWCNTs) with particle size ranging from 70 to 90 nm from the scanning transition electron microscopy (STEM) image in Figure 1a. The high-resolution TEM (HRTEM) image from the selected area (red dashed line frame) of one particle (inset of Figure 1b) in Figure 1b shows the arrays of lattice fringes. The inter-planar spacing between adjacent fringes are measured to be 0.204 nm and 0.176 nm, corresponding to (111) and (200) planes, respectively. The corresponding crystal planes in HRTEM image are consistent with the theoretical inter-planar spacing of NiCo$_2$/CNT from the XRD patterns (Figure S1c) where (111) and (200) lattice planes were detected at 44.3 ° and 51.7 °. According to Debye–Scherrer equation [39], the average crystal size of (111) plane for NiCo$_2$/CNT is 25.6 nm. Two pristine solid particles with different facet exposure are presented from the dark-field STEM image (DF-STEM) in Figure 1c. The corresponding STEM-electron energy loss spectroscopic (EELS) mapping from the two particles reveals the intermixing of nickel and cobalt in an ensemble of particles with nickel-rich surface, suggesting a surface segregation took place in Ar/H$_2$ atmosphere during the Ni-Co alloy formation [40]. Moreover, Co/CNT and Ni/CNT were obtained via the same method for comparison. The XRD patterns in Figure S1(a, b) confirmed the formation of pure metal phase.

**Figure 1** (a) Overview STEM image NiCo$_2$/CNT nanoparticles; (b) high resolution TEM image of part of one NiCo$_2$ particle (inset, scale bar is 20 nm); (c) elemental mappings of NiCo$_2$/CNT particles (scale bar is 50 nm).

Hollow structured NiCo$_2$O$_4$ particles with interconnected pores were formed via oxidizing the NiCo$_2$ alloy particles at 350 °C in air atmosphere. As shown from the XRD pattern (Figure S1c), the NiCo$_2$ particles were fully
oxidized to form oxides. Diffraction peaks at 18.9°, 31.2°, 36.7°, 44.6°, 59.1°, 64.9° correspond to (111), (220), (311), (400), (511) and (440) lattice planes, which are consistent with the standard diffraction pattern of NiCo$_2$O$_4$ (JCPDS No. 02-4211). Compared with the XRD pattern of NiCo$_2$/CNT, the crystal size decreased obviously, and the main crystal size of (311) plane is calculated to be 7.1 nm. The TGA curves (Figure S1d) showed that the weight percentage of the metal oxides were approximately 56%. The main atomic percentage of Ni and Co (Table S1) obtained from XRF results is about 35% and 65%, which is approximately 1 : 2, thus, the binary catalyst was definite as NiCo$_2$O$_4$/CNT. The hollow structure of NiCo$_2$O$_4$ particles were verified by STEM images in Figure 2a and TEM image in Figure S2. It can be seen that the 3D nanostructure of the NiCo$_2$O$_4$ particles featured by a series of internal cavities and hollow voids. The rough surface of NiCo$_2$O$_4$ is contrary to the NiCo$_2$ particle (smooth in surface). The average particle size is calculated to be about 80 nm by measuring more than 200 particles. Moreover, scanning electron microscopy (SEM) image in Figure S3 depicts that the particles are surrounded by CNTs which would enhance the electric-conductivity of the NiCo$_2$O$_4$/CNT composite. The inter-planar spacing between adjacent fringes in Figure 2b from part of a NiCo$_2$O$_4$ particle (inset of Figure 2b) are measured to be 0.287 nm, 0.245 nm and 0.203 nm, corresponding to (220), (311) and (400) planes, respectively. The enlarged TEM images in Figure 2e and the inset of Figure 2b reveal that the particles are likely to consist of small individual particles. The main crystal size was measured to be 7 nm (inset of Figure 2f), which is greatly consistent with the calculating results of (311) plane of NiCo$_2$O$_4$/CNT from the XRD patterns. The phenomenon is verified by the HRTEM image in Figure 2f which demonstrates that different adjacent fringes region (the white dotted line) can be clearly distinguished, indicating good crystal structure of NiCo$_2$O$_4$ particles. While the region with different adjacent fringes (Figure 2f) is probably caused by overlapping of different ultra-small particles. The formation of hollow structure was based on the Kirkendall effect, where the internal metal elements of NiCo$_2$ alloy would transfer to the outside and react with the oxygen outside the particle at proper temperature, and then after NiCo$_2$ particle was completely oxidized, the morphology was transformed into hollow structure. The formation of interconnected pores experienced two stages during the oxidation step according to the report of Xin and co-workers [41], in which hollow structure was first obtained via the oxidation step (left particle in Figure 2c) and then the subsequent immigration between Ni, Co and O atoms resulted in interconnected pores (right particle in Figure 2c). The chemical distribution of Ni and Co in the two particles (Figure 2c and Figure 2d) indicates that the oxidized particles are wrapped by a Co-rich surface layer. The different surface composition for NiCo$_2$ and NiCo$_2$O$_4$ particle is possibly due to the different reaction
atmosphere during the synthetic process [42]. Co$_3$O$_4$/CNT and NiO/CNT were obtained by oxidizing Co/CNT and Ni/CNT. The XRD patterns in Figure S1a shows characteristic diffraction peaks at 18.9°, 31.3°, 36.8°, 38.5°, 44.8°, 59.3° and 65.3°, and XRD patterns in Figure S1b exhibits featured diffraction peaks at 36.9°, 43.2°, 62.8°, 75.3° and 79.4°, which are consistent with the standard diffraction pattern of Co$_3$O$_4$ (JCPDS No. 42-1467) and NiO (JCPDS No. 01-0269), respectively. The morphology for the as-prepared Co$_3$O$_4$/CNT and NiO/CNT are proved to be hollow structure (Figure S4a and Figure S5a) with main particle size of 124 nm and 110 nm, respectively. The HRTEM image (Figure S4b) of Co$_3$O$_4$/CNT shows obvious (311) lattice planes with inter-planar spacing of 0.243 nm. Moreover, uniformly distribution of Co and O element can be detected from the Co$_3$O$_4$ particles in Figure S4c. The measured inter-planar spacing value of 0.208 nm and 0.147 nm from the HRTEM image of NiO/CNT (Figure S5b) are corresponding to (200) and (220) lattice planes, respectively.

Figure 2 (a) Overview STEM image of NiCo$_2$O$_4$/CNT nanoparticles; (b) high resolution TEM image of part of one NiCo$_2$O$_4$ particle (inset, scale bar is 20 nm); (c-d) enlarged STEM images of two single particles and the corresponding elemental mappings (scale bar is 50 nm); (e) enlarged TEM image of NiCo$_2$O$_4$/CNT nanoparticles; (f)
enlarged area of high resolution TEM image from the inset NiCo$_2$O$_4$ particle image in Figure 2b and the insets is the corresponding crystal size distribution histogram.

As anode materials for LIBs, the lithium storage properties of 3D NiCo$_2$O$_4$/CNT was evaluated by cyclic voltammetry (CV) examination for the first five cycles in the potential range of 0.05 to 3 V at a scan rate of 0.1 mV s$^{-1}$ (Figure 3a). The voltammogram for the first cycle is substantially different from those of the subsequent four cycles. An irreversible reduction cathodic peak was obtained at around 0.5 V, corresponding to the initial reduction of M$^{2+}$ to M and the formation solid electrolyte interphase (SEI), while peaking at around 0.96 V is ascribed to the reduction of M$_{3+}$ to M$^{2+}$ [43, 44]. The oxidation peak at 2.2 V in the anodic scan corresponds to the oxidation of metal to metal oxides and Li$_2$O decomposition. In the subsequent cycles, there remains only one cathodic peak which shifts to about 1.02 V due to the drastic Li$^+$ driven structural or textural modifications during the first lithiation process [45], Figure 3b described the initial five charge/discharge curves of NiCo$_2$O$_4$/CNT electrode at a current density of 0.2 A g$^{-1}$ and potential window from 0.05 V to 3.0 V. Results showed that the charge/discharge potential platform for the five groups of curves was well consistent with the redox peaks in CV curves. The first discharge potential platform of NiCo$_2$O$_4$/CNT was situated between the first discharge platform of Co$_3$O$_4$/CNT (1.09 V, see in Figure S6a) and NiO/CNT (0.71 V, see in Figure S6b), indicating that the combination of Ni and Co made good influence for the electrochemical performance. The discharge plateau increased in the subsequent curves, whereas the overall trend maintained. The initial discharge and charge capacities of NiCo$_2$O$_4$/CNT are 1656 mA h g$^{-1}$ and 1024 mA h g$^{-1}$, respectively, with an initial Coulombic efficiency (CE) of 62%. The irreversible capacity between the first discharge and charge process may be ascribed to the decomposition of electrolytes and the SEI film formation on the electrode surface. Afterwards, the capacity was maintained at around 1000 mAh g$^{-1}$. In comparison, Co$_3$O$_4$/CNT and NiO/CNT exhibited lower first discharge and charge capacities (1544 mAh g$^{-1}$ and 912 mAh g$^{-1}$ for Co$_3$O$_4$/CNT, 1434 mAh g$^{-1}$ and 741 mAh g$^{-1}$ for NiO/CNT, Figure S6a and Figure S6b) and CE (59% and 52% for Co$_3$O$_4$/CNT and NiO/CNT, respectively) than NiCo$_2$O$_4$/CNT.

In addition, the rate performance of NiCo$_2$O$_4$/CNT is shown in Figure 3c, in which the current density is increased stepwise from 0.2 A g$^{-1}$ to 5 A g$^{-1}$. Impressive high reversible capacities of 1108, 1005, 915, 805 and 643 mAh g$^{-1}$ were obtained at current densities of 0.2, 0.5, 1, 2 and 5 A g$^{-1}$. Notably, the capacity recovered and even exceeded the initial level when the current density is returned to 0.2 A g$^{-1}$. The increase of current density is mainly
attributed to the shorten of charge/discharge distance after transient activation process [21]. When compared with Co$_3$O$_4$/CNT and NiO/CNT, the rate performance of NiCo$_2$O$_4$/CNT exhibited much higher capacity and lower capacity change during current density change. Furthermore, the stability of the NiCo$_2$O$_4$/CNT electrodes at current densities of 0.5 and 1 A g$^{-1}$ are shown in Figure 3d. It can be seen that high reversible capacities of 1155 and 892 mA h g$^{-1}$ are obtained after 200 cycles (higher than Co$_3$O$_4$/CNT and NiO/CNT at a current density of 0.5 A g$^{-1}$, seen in Figure S6c), suggesting the excellent reversibility of discharge/charge properties under relative low/high current density. During the discharge/charge performance, the discharge capacity is nearly equal to the charge capacity at the same circle (CE value equals to ~99%), proving an excellent reversibility for the NiCo$_2$O$_4$/CNT. Meanwhile, the cycling stability of hollow structured NiCo$_2$O$_4$ and MWCNTs were also investigated as anodes for LiBs (Figure S7). The MWCNTs exhibited lower capacity of 155 mAh g$^{-1}$ at 0.5 A g$^{-1}$. After deducting the capacity of MWCNTs, the NiCo$_2$O$_4$/CNT also exhibited excellent cycling performance (higher than 900 mAh g$^{-1}$) at 0.5 A g$^{-1}$, higher than pure NiCo$_2$O$_4$, indicating that the incorporation of MWCNTs with NiCo$_2$O$_4$ would effectively enhance the electron transfer rate and then increase the battery capacity. Long-life cycling performance for high-rate LIBs remains a great challenge which appeals excellent electrode materials to accommodate such fast charge/discharge rate [46, 47].

Based on the merits of porosity, hollow, excellent crystal structure, high electric conductivity via CNT support and good characteristics for the binding of Ni and Co, the NiCo$_2$O$_4$/CNT exhibited excellent long-term cycling stability at a current density as high as 5 A g$^{-1}$ for more than 4000 cycles. As is shown in Figure 3e, high reversible capacity of 500 mA h g$^{-1}$ is obtained after 4000 cycles, with average CE value of above 99%, confirming the excellent high-rate stability performance during discharge/charge processes. Compared with the cycling performances at relative lower discharging/charging rate of the recent reported NiCo$_2$O$_4$ based electrodes as LIBs anode system listed in literatures (Table S3), the hollow structured NiCo$_2$O$_4$/CNT presented are ranked in the front row. In addition, the excellent long-cycling life performance at high discharging/charging rate (5 A g$^{-1}$) of hollow structured NiCo$_2$O$_4$/CNT showed great potential in next generation LIBs.
Figure 3 (a) Cyclic voltammogram curves of NiCo$_2$O$_4$/CNT at a scan rate of 0.1 mV s$^{-1}$; (b) discharge/charge profiles of NiCo$_2$O$_4$/CNT for the first five cycles at a current density of 0.2 A g$^{-1}$; (c) Rate performance of NiCo$_2$O$_4$/CNT at different current densities between 0.2 and 5 A g$^{-1}$; (d) Cycling performance of NiCo$_2$O$_4$/CNT at current densities of 0.5 A g$^{-1}$ and 1 A g$^{-1}$; (e) Long-term discharge performance of NiCo$_2$O$_4$/CNT at current density of 5 A g$^{-1}$ and corresponding CE value.

To gain insight of the excellent electrochemical performance of 3D NiCo$_2$O$_4$/CNT nanocomposite, electrochemical impedance spectrometry (EIS) was performed. The Nyquist plots in Figure 4a clearly shows that the cell assembled by using NiCo$_2$O$_4$/CNT as electrode material exhibited the smallest semicircle diameter compared with Co$_3$O$_4$/CNT and NiO/CNT (the values can be seen from Table S2), indicating a better charge transfer...
performance and electric-conductivity of 3D NiCo$_2$O$_4$/CNT (The equivalent circuit model can be seen in Figure S8). Compared with the semicircle diameter of NiCo$_2$O$_4$/CNT, bare NiCo$_2$O$_4$, MWCNTs and the mechanic mixture of NiCo$_2$O$_4$ and MWCNTs (Figure S9), the electric-conductivity of 3D NiCo$_2$O$_4$/CNT was situated much closer to MWCNTs than NiCo$_2$O$_4$ and the mechanic mixture of NiCo$_2$O$_4$ and MWCNTs, indicating the great significance of the combination of NiCo$_2$O$_4$ with MWCNTs. The results indicated that the combination of Ni and Co enhanced the electronic conductivity. Besides, the diameter of the semicircle remained slightly changed on NiCo$_2$O$_4$/CNT electrode after 200 cycles at a current density of 1 A g$^{-1}$ (Figure 4b), indicating the excellent charge transfer stability, which also explained the excellent long-term performance for 4000 cycles at high-rate current density of 5 A g$^{-1}$. In addition, CV measurements at scan rates ranging from 0.1 to 5 mV s$^{-1}$ were performed to better understand the underlying reasons for the superior high rate capability of 3D NiCo$_2$O$_4$/CNT [48]. As shown in Figure 4c, well-defined peaks at different scan rates are observed where the anodic peaks shift to the higher potential and the cathodic peaks move to the lower potential with the increasing of scan rates. The fitting line of log (i) to log (ν) was plotted according to the CV curves in Figure 4c, where i represents the cathodic peak current, ν is the scan rate. The relationship of current to scan rate comply with power law dependence function below:

$$i = av^b$$ \hspace{1cm} (1)

According to equation (1), the power coefficient b is indicative of the charge storage kinetics in the electrode which also represents the slope value for the fitting line in Figure 4d. Thus, it clearly demonstrates that the cathodic current exhibits a linear dependence with a slope value of 0.71, indicating a fast, surface controlled kinetics corroborating the high counter-ion mobility and ultra-fast electron transfer kinetics of the electrode [49, 50]. Thus, it can be speculated that the excellent kinetics of the NiCo$_2$O$_4$/CNT electrode was ascribed to the high electronic conductivity of carbon nanotubes, the second-level structure of small crystals and the hollow structure with interconnected pores.
Figure 4 (a) Nyquist plots of fresh cell using NiCo$_2$O$_4$/CNT, Co$_3$O$_4$/CNT and NiO/CNT as electrode materials; (b) Nyquist plots of NiCo$_2$O$_4$/CNT electrode before and after 200 cycles at current density of 1 A g$^{-1}$; (c) Cyclic voltammogram curves of NiCo$_2$O$_4$/CNT at scan rates from 0.1 mV s$^{-1}$ to 5 mV s$^{-1}$; (d) Cathodic peak current function of the scan rate for the NiCo$_2$O$_4$/CNT electrode.

According to the electrochemical performance of the 3D NiCo$_2$O$_4$/CNT nanocomposite, the hollow structure with interconnected pores was speculated to play an important role in the whole process, which not only provided adequate space to accommodate the volume change during the lithiation process, but also maintained the structural integrity after delithiation process, shorten the lithiation distance (seen from the Schematic image in Figure 5a). In addition, the NiCo$_2$O$_4$ particles surrounded by high electric-conductive MWCNTs would enhance the electrons transfer rate. Therefore, to verify the speculation, the structural change on different lithiation and delithiation states for NiCo$_2$O$_4$ particles were monitored via ex-situ STEM study during the first cycle. As shown in Figure 5b, the original NiCo$_2$O$_4$ particle exhibited hollow structure and small holes, while after a half-lithiation process, the voids in the particle was fully filled with Li$_2$O and transition metal (Figure 5c), leading to the expansion of the particle size. After a whole discharging process, obvious small particle can be seen (Figure 5d) which may be caused by the
aggregation of transition metal or Li$_2$O via the further process of lithium insertion. The subsequent half-delithiation STEM image in Figure 5e shows a crescent shaped (red dashed box) bright area, which presents the remaining Li$_2$O in the particle. Therefore, it is concluded that the hollow structure of NiCo$_2$O$_4$ particle can be maintained after discharge/charge process. It should be noted from Figure 5f that the hollow structure was still maintained even after 200 cycles at a current density of 1 A g$^{-1}$. Furthermore, the lattice fringes can be seen clearly in Figure 5g and the measured inter-planar spacing value is 0.245 nm, corresponding to the (311) plane of NiCo$_2$O$_4$, indicating a stable crystal structure of NiCo$_2$O$_4$. Thus, it can be concluded that the hollow structure in the particles with interconnected pores not only provide enough space for adapting the volume change, but also shorten the transport length for Li ions during lithiation/delithiation, favoring cycling stability and high-rate capability.

Figure 5 (a) Schematic of the lithiation and delithiation process of NiCo$_2$O$_4$ particle with interconnected pores. (b-g) STEM image of NiCo$_2$O$_4$ particle at different lithiation or delithiation state. Original hollow particle (b); half-discharge state (c); fully discharge state (d); half charge state (e); after 200 cycles at current density of 1 A g$^{-1}$ (f); HRTEM image after 200 cycles at current density of 1 A g$^{-1}$ (g).
4. Conclusions

In conclusion, 3D NiCo$_2$O$_4$/CNT bimetallic oxide materials have been successfully prepared via a simple two-step method. The NiCo$_2$O$_4$/CNT electrode material present hollow structure with interconnect pores and consists of small individual particles with good crystal structure. The unique structure shortened the pathways for Li ion diffusion and provided sufficient surface area to accommodate the volume change during the charge/discharge processes. Such a 3D hollow structure maintained the electrode material electrochemically active without sacrificing template or using surfactants during the synthetic approach. As a result, benefiting from such unique structure and Ni-Co incorporation, the 3D NiCo$_2$O$_4$/CNT outperformed Co$_3$O$_4$/CNT and NiO/CNT, exhibited superior rate performance and long-term high-rate stability at current density of 5 A g$^{-1}$ for more than 4000 cycles as anode material for LIBs.

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Carbon nanotube supported hollow structured NiCo$_2$O$_4$ nanoparticles with interconnected pores were fabricated via a simple one-pot method which possess excellent charge storage kinetics and exhibited ultra-high discharge/charge stability for 4000 cycles at a high-rate current density of 5 A g$^{-1}$, when used as anode material for the lithium ion battery.
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