In-situ Synthesis and Unprecedented Electrochemical Performance of Double Carbon Coated Cross-linked Co$_3$O$_4$

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ABSTRACT

Improving the structural stability and the electron/ion diffusion rate across whole electrode particles is crucial for transition metal oxides as next-generation anodic materials in lithium ion batteries. Herein, we report a novel structure of double carbon coated Co$_3$O$_4$ cross-linked composite, where Co$_3$O$_4$ nanoparticle is in-situ covered by nitrogen-doped carbon and further connected by carbon nanotubes (Co$_3$O$_4$ NP@NC@CNTs). This double carbon coated Co$_3$O$_4$ NP@NC@CNTs framework not only endows a porous structure that can effectively accommodate the volume changes of Co$_3$O$_4$, but also provides multidimensional pathways for electronic/ionic diffusion in and among the Co$_3$O$_4$ nanoparticles. As expected, the Co$_3$O$_4$ NP@NC@CNTs electrode exhibits unprecedented lithium storage performance, with high reversible capacity of 1017 mAh g$^{-1}$ after 500 cycles at 1 A g$^{-1}$, and very good capacity retention of 75%, even after 5000 cycles at 15 A g$^{-1}$. The lithiation/delithiation process of Co$_3$O$_4$ NP@NC@CNTs is dominated by pseudocapacitive behavior, resulting in excellent rate performance and durable cycle stability. Electrochemical kinetics further reveals a decreased energy barrier for electron/ion transport, synergistically, contributes to its excellent lithium storage performance.

1. Introduction

Transition metal oxides (TMOs, M = Zn, Co, Fe, Ni, etc.) have received intense interest as potential anodic materials for lithium ion batteries (LIBs), owing to their high theoretical capacity and natural abundance.$^{1-5}$ The practical applications of TMOs, however, are hindered by the following reasons. a) Severe volume changes (e.g. ~100 % for Co$_3$O$_4$) during the Li$^+$ insertion/extraction cycles, resulting in electrode pulverization and finally peeling off from the current collector, leading to irreversible capacity loss. b) Poor rate performance that is based in the nature of TMOs
and their discharge mixture (TM/Li$_2$O). To date, various efforts have been devoted to address the above issues.$^6$-$^{10}$ In particular, embedding TMOs into carbon matrix has attracted enormous interest.$^{12}$-$^{15}$ For example, Yang et al. reported excellent electrochemical performance of their ZnO nanoparticles (NPs)@nitrogen-doped carbon (NC) hybrids$^1$. Our group reported the superior sodium storage performance of zeolitic imidazolate framework-67 (ZIF-67) derived Co$_3$O$_4$ NP@NC hybrid.$^{16}$ Although great achievements have been obtained, a key disadvantage of these single carbon/TMOs is their limited interfacial conductivity and connectivity between individual carbon/TMO particles, which results in relatively low utilization of the TMO NPs.$^{17,18}$ It is, therefore, crucial to introduce an “intermediary” to reinforce the conductive contact between different electrode particles.$^{[Liu, 2015 #3317;Guo, 2015 #3321;Wang, 2016 #3344]}$. However, the investigation about such dual carbon coated electrode is still in its infancy.

Carbon nanotubes (CNTs), which exhibit great mechanical strength and excellent electrical conductivity, are an ideal candidate to act as intermediary.$^{[Wu, 2013 #3320]}$ Electrodes with CNTs such as Fe$_3$C@N–CNTs,$^{19}$ ZnO@NC@CNTs hybrids,$^{20}$ and NiP$_2$@C-CNTs,$^{21}$ have shown enhanced electrochemical performance. Recently, Chen et al. reported an in-situ synthesized “sea urchin” like Co NPs@CNTs framework by using ZnCo-MOFs as precursor, and confirmed that the interconnected CNTs could facilitate both local and interfacial electron transportation in the electrode.$^{22}$ To date, many works have focused on the TMO NPs@carbon or TMO NPs@CNTs hybrids, however, the structural superiority of TMO NPs@carbon@CNTs formed in-situ has been ignored.

Inspired by the above considerations and the feasibility of growing CNTs in-situ by a proper pyrolysis process, herein, we designed a novel structure that connected the Co$_3$O$_4$ NPs@NC units in-situ by CNTs. Through a pyrolysis-oxidation strategy a simple ZIF-67 precursor was converted
to Co$_3$O$_4$ NPs (3–7 nm) that were covered by NC layers, and further connected by intertwined CNTs, forming a unique double carbon coated Co$_3$O$_4$ NP@NC@CNTs framework. On the one hand, the ultra-small Co$_3$O$_4$ NP@NC units effectively shorten the electronic/ionic diffusion distances and alleviate the electronic/ionic conductivity of a single unit. On the other hand, the interconnected CNTs enhance the conductive contact between different Co$_3$O$_4$ NP@NC units. In addition, the porous structure of the Co$_3$O$_4$ NP@NC@CNTs can effectively accommodate the volume changes and facilitate better contact between the electrolyte and the electrode. Therefore, unprecedented electrochemical performance is observed in the Co$_3$O$_4$ NP@NC@CNTs based electrode, which shows high reversible capacity, excellent rate capability, and extraordinary cycling stability under super-high current densities. In particular, high capacities of 1017 and 235 mAh g$^{-1}$ are delivered at 1.0 and 15 A g$^{-1}$ after 500 and 5000 cycles, respectively. To the best of our knowledge, such outstanding electrochemical performance had been rarely reported for Co$_3$O$_4$-based anodic materials in LIBs. Although metal-organic frameworks (MOFs) have been used as precursors to obtain TMO NPs@carbon hybrids,$^{12-15}$ further improvement to synthesis such double carbon coated TMOs is still in its infancy due to the limited reports on this research field. Therefore, our work may shed light on novel designs for other TMO-based electrodes with high electrochemical performance.

2. Experimental Section

2.1 Synthesis of Co$_3$O$_4$ NP@NC@CNTs networks: The Co$_3$O$_4$ NP@NC@CNTs networks were derived by first converting ZIF-67 into Co NP@NC, followed by annealing under an Ar/C$_2$H$_2$ gas mixture (10% C$_2$H$_2$), and then oxidizing to Co$_3$O$_4$ NP@NC@CNTs. Briefly, the ZIF-67 derived Co NP@NC was synthesized according to our previous report$^1$. Then, the Co NP@NC powders
were transferred into a tube furnace and heated to 600 °C (ramp rate: 10 °C min⁻¹), and then held for 30 min under the Ar/C₂H₂ gas mixture. After naturally cooling down to room temperature, the resultant sample was further oxidized at 200 °C for 24 h in air. The target sample is denoted as Co₃O₄ NP@NC@CNTs. ZIF-67 derived Co₃O₄ NP@NC was synthesized by directly oxidized the Co NP@NC, under same conditions as the Co₃O₄ NP@NC@CNTs.

2.2 Structural and physical characterization: X-ray diffraction (XRD, Rigaku D/Max-2500, Cu Kα radiation), field-emission scanning electron microscopy (FESEM, JEOL, SU8010), transmission electron microscopy (TEM), high-resolution TEM (HRTEM, JEOL JEM-2010FEF), thermogravimetric analysis (TGA, TA-Q50), N₂ adsorption/desorption isotherms (Quantachrome, Autosorb-IQ2-VP), X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI), and Raman spectroscopy (Renishaw inVia, excitation 514.5 nm) were employed for morphological and structural investigations. The electrical conductivity of samples was tested based on a four-probe system (RST-9).

2.3 Electrochemical testing: The electrochemical performance of samples were evaluated by assembling 2032 coin cell batteries. Typically, active materials, conductive carbon black, and polyvinylidene fluoride (PVDF) were mixed in a weight ratio of 8:1:1, dispersed in N-methyl-2-pyrrolidone (NMP), and then milled for 30 min to form a slurry. The slurry was cast onto copper foil using a doctor blade, and vacuum dried at 80 °C overnight. The loading mass of Co₃O₄ NP@NC and Co₃O₄ NP@NC@CNTs is around 0.9 and 0.8 mg cm⁻², respectively. Lithium discs (MTI Corporation) were used as the counter electrode. 1 M LiPF₆ (Sigma Aldrich) in ethylene carbonate (EC, Sigma Aldrich), diethyl carbonate (DEC, Alfa Aesar), and fluorinated ethylene carbonate (FEC, Sigma Aldrich) (volume ratio 6:3:1) was used as the electrolyte. Polypropylene (PP, MTI Cooperation) was used as the separator. The cells were assembled in an argon-filled
glove box with the oxygen and water content below 0.1 ppm. Galvanostatic charge-discharge tests were carried out at room temperature on a battery testing system (LAND Wuhan, China) in the potential range of 0.01−3.00 V (vs. Li/Li⁺). Cyclic voltammetry (CV) tests and electrochemical impedance spectroscopy (EIS) measurements were performed on a CHI660E electrochemical workstation. The specific capacity in this work were calculated based on Co₃O₄ NP@NC or Co₃O₄ NP@NC@CNTs.

3. Results and Discussion

![Figure 1.](image)

**Figure 1.** (a) Schematic illustration for the synthesis procedure of Co₃O₄ NP@NC@CNTs framework. (b) XRD pattern, (c) Raman spectrum, (d) TGA curve (in air), and high resolution XPS spectra of (e) C 1s, (f) N 1s, and (g) Co 2p peaks of Co₃O₄ NP@NC@CNTs.
Synthesis procedure for the Co$_3$O$_4$ NP@NC@CNTs framework is illustrated in Figure 1a. By pyrolyzing the ZIF-67 precursors in Ar, the surfaces of the polyhedra changed from smooth to rough (Figure S1 in the Supporting information), indicating formation of the Co NP@NC subunits (Figure S2). Subsequently, Co in the Co NP@NC units catalyzed the growth of CNTs under an Ar/C$_2$H$_2$ mixture gas. Meanwhile, when annealed the Co NP@NC at 600 °C in Ar for 30 min, no CNTs was observed (Figure S3), further confirming that CNTs in Co$_3$O$_4$ NP@NC@CNTs is generated by the decomposition of C$_2$H$_2$. After a careful oxidation process in air, the unique Co$_3$O$_4$ NP@NC@CNTs framework obtained. The good permeation of Ar/C$_2$H$_2$ resulted in homogeneous CNTs growth in the resultant sample (Figure S1e, f). A ZIF-67 derived Co$_3$O$_4$ NP@NC framework was also prepared for comparison.

XRD pattern of the Co$_3$O$_4$ NP@NC@CNTs framework displays several peaks at 31.0°, 36.6°, 38.2°, 44.4°, 52.2°, 58.8°, and 64.7°, that can be ascribed to the (220), (311), (222), (400), (422), (511), and (440) planes of cubic Co$_3$O$_4$ (JCPDS No. 80-1544), respectively (Figure 1b). The broad peak at 23.8° is attributed to the (002) planes of graphitic carbon. Notably, the diffraction peaks of Co$_3$O$_4$ are broad and weak, indicating small crystal size. The Raman spectrum was used to acquire more structural information on the Co$_3$O$_4$ NP@NC@CNTs framework (Figure 1c). The typical Co$_3$O$_4$ mode vibrations $F_{2g}$, $E_g$, $F_{2g}$, $F_{2g}$, and $A_{1g}$ are observed. Meanwhile, the typical D band (1325 cm$^{-1}$) for disordered carbon and the G band (1591 cm$^{-1}$) for graphitic carbon are present, in agreement with the co-existence of amorphous NC and CNTs. For the Co$_3$O$_4$ NP@NC sample, the D band and G band are located at 1328 and 1594 cm$^{-1}$, respectively (Figure S3). The slight shift of these bands in Co$_3$O$_4$ NP@NC@CNTs indicates good connections between the Co$_3$O$_4$ NP@NC units and the CNTs. The TG curve (Figure 1d) indicates a total weight loss of 44 wt.% in air, causes
by evaporation of NC and CNTs in the Co₃O₄ NP@NC@CNTs. The Co₃O₄ NP@NC lost only 26 wt.% under same conditions (Figure S4). Therefore, the Co₃O₄ NP@NC@CNTs is composed of about 18 wt.% CNTs, 26 wt.% NC, and 56 wt.% Co₃O₄ NPs.

The XPS spectra reveal the chemical states of C, N, and Co (Figure 1e–g). The deconvolution of the C 1s spectrum reveals four peaks at 284.6, 285.2, 286.6, and 288.6 eV, corresponding to the $sp^2$ C-C, $sp^2$ C-N, $sp^3$ C-N, and C-O (physical absorption) bonds, respectively. The N 1s spectrum has four components centered at 398.9, 400.1, 401.1, and 401.9 eV, representing pyridinic N, pyrrolic N, graphitic N, and oxidation N, respectively.

Pyridinic and pyrrolic N are dominant in Co₃O₄ NP@NC@CNTs, which is believed to be of benefit for the electrolyte wettability and provide better conductivity. The spectrum of Co 2p exhibits two dominant peaks at 780.3 and 795.5 eV, representing the 2p₁/₂ and 2p₃/₂ peaks of Co₃O₄. The XPS results are in agreement with the XRD patterns and Raman analysis.

TEM images of Co₃O₄ NP@NC@CNTs are shown in Figure 2a and b. The Co₃O₄ NP@NC@CNTs maintains the polyhedral outline of the ZIF-67 precursor and displays a uniform particle size of ~150 nm. Unlike Co₃O₄ NP@NC (Figure S5), abundant CNTs are observed in the Co₃O₄ NP@NC@CNTs (Figure 2a). Figure 2b shows that the outer diameter of the CNTs ranges from 9 to 12 nm, and the Co₃O₄ NP@NC units are wrapped by CNTs. HR-TEM (Figure 2c, d) images better represent the architecture of Co₃O₄ NP@NC@CNTs. The lattice spacing of 0.28 nm at point A corresponds to the (220) planes of cubic Co₃O₄. The short and curved lattice fringes with a d-space of 0.37 nm at point B are associated with the (002) planes of NC. CNTs that covering the Co₃O₄ NP@NC units are marked as C, which show an expanded (002) interplanar space of 0.42 nm, causing by the relative lower formation temperature and/or short annealing time. Small graphitic layers are randomly stacked forming the walls of CNTs, which indicated more defects.
Furthermore, abundant mesopores (point D) can be found inside the Co₃O₄ NP@NC@CNTs framework. Bright spots assigned to Co₃O₄ NPs (about 3–7 nm in diameter) are observed in the high-angle annular dark field mode (HAADF, Figure 2e). The energy dispersive X-ray spectroscopy (EDX, Figure 2f)) spectrum demonstrates the homogeneous distribution of Co, O, C, and N in the framework. The porous nature of Co₃O₄ NP@NC@CNTs was examined by N₂ isotherms (Figure S6a). A type IV hysteresis loop is observed, indicating that the Co₃O₄ NP@NC@CNTs has a mesoporous structure. The specific surface area of Co₃O₄ NP@NC@CNTs is 372 m² g⁻¹, larger than the 101 m² g⁻¹ for Co₃O₄ NP@NC (Figure S6b). The larger surface area of Co₃O₄ NP@NC@CNTs is caused by the intertwined CNTs, which is of benefit for the charge and mass transport in the electrode.
**Figure 2.** Morphology and architecture characterization of Co$_3$O$_4$ NP@NC@CNTs. (a, b) TEM, (c, d) HR-TEM, and (e) HAADF mode images, and (f) EDX elemental mapping of N, Co, O, and C, corresponding to the red square in (e). The scale bar in (e) is 100 nm. (g) and (h) illustrate the lithiation process for the Co$_3$O$_4$ NP@NC and Co$_3$O$_4$ NP@NC@CNTs frameworks.

Figure 2g, h illustrates the structural superiority of this double carbon coated Co$_3$O$_4$ NP@NC@CNTs framework. Although the NC layer in the Co$_3$O$_4$ NP@NC sample improves the conductivity of the individual Co$_3$O$_4$ NPs, the poor contact between different Co$_3$O$_4$ NPs is
unfavorable for electron/Li$^+$ transport, which results in low utilization of the electrode.$^{17,18}$ In the case of Co$_3$O$_4$ NP@NC@CNTs, the Co$_3$O$_4$ NP@NC units are distributed along the CNTs, forming multidimensional pathways for efficient electron/Li$^+$ transport. The CNT skeleton can not only provide multidimensional channels for rapid electron/ion transport in/among the Co$_3$O$_4$ NP@NC units, but also effectively buffers the stress during volume expansion/shrinkage, resulting in excellent rate ability and cycling stability. In addition, the in-situ grown CNTs provide a large contact area between the electrolyte and the electrode.

The electrochemical performance of this novel Co$_3$O$_4$ NP@NC@CNTs electrode was investigated, and compared with ZIF-67 derived Co$_3$O$_4$ NP@NC. The first lithiation process of Co$_3$O$_4$ NP@NC (Figure 3a) results in a small peak at $\sim$1.0 V that is assigned to reduction of Co$^{3+}$ to Co$^{2+}$, and a dominant peak at $\sim$0.8 V that reflects reduction of Co$^{2+}$ to Co and the formation of a solid electrolyte interphase (SEI) film.$^{30,31}$ The anodic peak at $\sim$2.1 V is associated with oxidation of Co to Co$^{2+}$. During the following cycles, the reduction peak of Co$^{2+}$ shifts to $\sim$1.1 V, which is caused by the dispersion of Co into the Li$_2$O matrix.$^{32}$ The Co$_3$O$_4$ NP@NC@CNTs shows similar cathodic and anodic peaks (Figure 3b). The stronger and more stable peaks in Co$_3$O$_4$ NP@NC@CNTs suggest higher Li$^+$ storage and easier electrochemical kinetics.$^{23}$ Figure S7 compares the initial four discharge/charge profiles of Co$_3$O$_4$ NP@NC@CNTs and Co$_3$O$_4$ NP@NC. In the first cycle, Co$_3$O$_4$ NP@NC@CNTs delivers a discharge and charge capacity of 1559 and 1011 mAh g$^{-1}$, respectively, much higher than that of Co$_3$O$_4$ NP@NC (1294 and 892 mAh g$^{-1}$ for discharge and charge), confirming better utilization of the Co$_3$O$_4$ NP@NC@CNTs electrode. The irreversible capacity loss in the first cycle may be caused by the formation of the SEI film and the irreversible reduction of Co$_3$O$_4$. In the subsequent cycles, the Coulombic efficiency (CE) reaches $\sim$100%, indicating high stability of the electrode. A significant difference between the discharge/charge
profiles of Co$_3$O$_4$ NP@NC@CNTs and Co$_3$O$_4$ NP@NC is the capacity contribution below 0.5 V. The Co$_3$O$_4$ NP@NC@CNTs shows ~416 mAh g$^{-1}$ in the voltage range of 0.01−0.5 V, while Co$_3$O$_4$ NP@NC delivers 341 mAh g$^{-1}$. The extra capacity of Co$_3$O$_4$ NP@NC@CNTs in this voltage range is attributed to the contribution of CNTs, which provide more active sites for Li$^+$ storage.

Figure 3. Cyclic voltammetry curves for the initial four cycles of (a) Co$_3$O$_4$ NP@NC, and (b) Co$_3$O$_4$ NP@NC@CNTs, from 0.01 to 3.0 V vs. Li/Li$^+$. (c) Rate capability of Co$_3$O$_4$ NP@NC@CNTs and Co$_3$O$_4$ NP@NC at various current densities, from 0.1 to 1 A g$^{-1}$, and (d) cycling performance of Co$_3$O$_4$ NP@NC@CNTs and Co$_3$O$_4$ NP@NC at 1.0 A g$^{-1}$ after the rate capability test.

Figure 3c displays the rate performance of Co$_3$O$_4$ NP@NC@CNTs and Co$_3$O$_4$ NP@NC. During the initial 10 cycles at 0.1 A g$^{-1}$, the capacity of Co$_3$O$_4$ NP@NC@CNTs gradually increases to
1427 mAh g\(^{-1}\), which may be due to continuous activation.\(^{35}\) The discharge capacity of Co\(_3\)O\(_4\) NP@NC@CNTs is maintained at about 1413, 1314, 1100, and 1074 mAh g\(^{-1}\) at 0.2, 0.4, 0.8, and 1.0 A g\(^{-1}\), respectively. Although capacity of the Co\(_3\)O\(_4\) NP@NC electrode is comparable to that of the Co\(_3\)O\(_4\) NP@NC@CNTs at low current, the superiority of the Co\(_3\)O\(_4\) NP@NC@CNTs becomes clear at high current. The cycling performance at 1.0 A g\(^{-1}\) is presented in Figure 3d. The Co\(_3\)O\(_4\) NP@NC@CNTs still delivers 1017 mAh g\(^{-1}\) after 500 cycles, demonstrating its excellent capacity retention (95%). The electrochemical performance of Co\(_3\)O\(_4\) NP@NC@CNTs is much better than the Co\(_3\)O\(_4\) NP@NC and other composites reported in the literature, as shown in Table S1, indicating the structural superiority of the Co\(_3\)O\(_4\) NP@NC@CNTs framework.

The amazing electrochemical performance of the Co\(_3\)O\(_4\) NP@NC@CNTs electrode inspired further electrochemical investigation at ultrahigh current densities (1.0−15 A g\(^{-1}\), Figure 4a). The Co\(_3\)O\(_4\) NP@NC@CNTs is able to deliver high capacities of 989, 924, 758, 618, and 537 mAh g\(^{-1}\) at current densities of 1.0, 2.0, 4.0, 6.0, and 8.0 A g\(^{-1}\), respectively. Even at 10 and 15 A g\(^{-1}\), this electrode can still deliver 459 and 321 mAh g\(^{-1}\). Moreover, when the current density returned to 1.0 A g\(^{-1}\), a high reversible capacity of 1140 mAh g\(^{-1}\) recovered. Detailed capacity retention of this Co\(_3\)O\(_4\) NP@NC@CNTs electrode at various current densities is given in Figure 4b. The long-life cycling performance of Co\(_3\)O\(_4\) NP@NC@CNTs at 15 A g\(^{-1}\) is presented in Figure 4c. High capacity of 240 mAh g\(^{-1}\) is still delivered after 5000 cycles at this super-high current density, corresponding to 75% capacity retention. The excellent structural stability of Co\(_3\)O\(_4\) NP@NC@CNTs is further confirmed by its CE, which remains at ~100% during the 5000 cycles (except for the first cycle).

The electrochemical performance comparison of this Co\(_3\)O\(_4\) NP@NC@CNTs with other highly studied Co-based electrodes in Figure 4d further demonstrates its superiority. The Co\(_3\)O\(_4\) NP@NC@CNTs shows 95% capacity retention at 1 A g\(^{-1}\) after 500 cycles, and 75% capacity
retention even at 15 A g$^{-1}$ after 5000 cycles, outperforming most other reported results.$^{33-38}$

![Graph showing electrochemical performance](image)

**Figure 4.** Electrochemical investigation of Co$_3$O$_4$ NP@NC@CNTs electrode. (a) High rate performance from 1.0 to 15 A g$^{-1}$, (b) capacity retention at different current densities, (c) long-life cycling performance at 15 A g$^{-1}$, (d) comparison of capacity retention and cycling performance between Co$_3$O$_4$ NP@NC@CNTs and other Co-based electrodes.

To understanding the kinetics mechanisms of such excellent electrochemical performance,
electrochemical impedance spectroscopy (EIS) analysis of Co$_3$O$_4$ NP@NC and Co$_3$O$_4$ NP@NC@CNTs was carried out. As demonstrated in Figure 5a and b, all the Nyquist plots contain a semicircle that is related to the charge transfer resistance ($R_{ct}$) and a sloping line that is related to the Warburg diffusion process. As the testing temperature is increased to higher values, the $R_{ct}$ decreases to lower values, indicating faster charge transfer kinetics. In addition, the Co$_3$O$_4$ NP@NC@CNTs shows a smaller semicircle than that of Co$_3$O$_4$ NP@NC (at the same temperature), meaning lower $R_{ct}$ resistance in the electrochemical reactions, which contributes to an easier electrochemical process. The apparent activation energy ($E_a$) for lithiation of both samples was calculated according to the following Equations:  

$$i_0 = \frac{RT}{nFR_{ct}} \quad (1)$$

$$i_o = Aexp\left(\frac{E_a}{RT}\right) \quad (2)$$

where $i_0$ is the exchange current, $A$ is a temperature independent coefficient, $R$ is the ideal gas constant, $T$ is the absolute temperature, $n$ is the number of transferred electrons, and $F$ is the Faraday constant. Figure 5c shows the Arrhenius plots of Co$_3$O$_4$ NP@NC and Co$_3$O$_4$ NP@NC@CNTs, where $E_a$ equals to the slope of the fitting curve multiplied by $R$. Detailed data for the Arrhenius fitting is given in Table S2. The $E_a$ is 63.7 kJ mol$^{-1}$ for Co$_3$O$_4$ NP@NC and 62.9 kJ mol$^{-1}$ for Co$_3$O$_4$ NP@NC@CNTs. The lower $E_a$ value of Co$_3$O$_4$ NP@NC@CNTs indicates a more facile lithiation process.

To further investigate the electrochemical kinetics of this novel double carbon coated structure, a CV test was performance at different scan rate. As shown in Figure 5d, all the peak currents ($i$) increase as the scan rates ($v$) increase. Generally, the scan rate and the measured current obey following laws, given in Equation 3-4.

$$i = av^b$$  

(3)
\[ \log i = b \times \log v + \log a \quad (4) \]

\[ i = k_1 v^{1/2} + k_2 v \quad (5) \]

Herein, \( a \) and \( b \) stand for empirical parameters. When \( b \) is close to 0.5, the electrochemical performance is dominated by a Faradaic process; when \( b \) is close to 1.0, the system features pseudocapacitive behavior. When applying the reduction peak (at 1.1 V) and the oxidation peak (at 2.1 V) to Equation 4, the \( b \)-values at different stage are calculated (Figure 5e). The high \( b \)-value at lithiation (0.73) and delithiation (0.81) process indicates the existence of pseudocapacitive behavior, which is positive for faster kinetics. The contribution ratio of pseudocapacitive behavior could be determined according to Equation 5. Normally, \( k_1 \) and \( k_2 \) is obtained by plotting \( i/v^{1/2} \) versus \( v^{1/2} \). At a given scan rate, the total capacitive contribution includes two parts: the one from diffusion-controlled fraction (\( k_1 v^{1/2} \)), and the one from capacitor-like fraction (\( k_2 v \)). Figure 5f summarizes contribution ratios of the pseudocapacitive behavior at various scan rates. The results demonstrate that pseudocapacitive charge-storage amount contributes a high percentage of the whole capacity.

The unique structure of \( \text{Co}_3\text{O}_4 \text{NP@NC@CNTs} \) enables excellent cycling stability and ultrafast rate capability. Firstly, the small particle sizes of the \( \text{Co}_3\text{O}_4 \text{NPs} \) effectively shorten the ion diffusion distance and alleviate the problem of structural collapse during lithiation/delithiation processes. Secondly, the interconnected porous \( \text{NC@CNTs} \) host effectively accommodates the volume expansion of \( \text{Co}_3\text{O}_4 \text{NPs} \) and also enhances conductivity. Thirdly, the interconnected CNTs can strengthen the structural stability of the \( \text{Co}_3\text{O}_4 \text{NP@NC units} \) and enhance the conductive contact between different active particles, resulting in better utilization of the active materials.
Figure 5. Nyquist plots of (a) Co$_3$O$_4$ NP@NC and (b) Co$_3$O$_4$ NP@NC@CNTs, at different temperatures, (c) the corresponding Arrhenius fitting plots of Co$_3$O$_4$ NP@NC and Co$_3$O$_4$ NP@NC@CNTs electrodes. (d) CV curves of Co$_3$O$_4$ NP@NC@CNTs at different scan rates from 0.5 to 1.3 mV s$^{-1}$, (e) the relationship between peak current and scan rate of Co$_3$O$_4$ NP@NC@CNTs at the reduction and oxidation process, (f) the normalize contribution ratio of pseudocapacitive behavior at different scan rate of Co$_3$O$_4$ NP@NC@CNTs.

4. Conclusion

In summary, a novel structure of Co$_3$O$_4$ NP@NC@CNTs, where Co$_3$O$_4$ NPs is covered by NC layers and further connected by CNTs, was synthesized by elaborately pyrolyze the ZIF-67 as precursor. The designed Co$_3$O$_4$ NP@NC@CNTs shows impressive potential for ultrafast LIBs in terms of high reversible capacity, long cycling stability, and very good capacity retention at high current density. To be specific, the high reversible capacity of 1017 mAh g$^{-1}$ was delivered after
500 cycles at 1.0 A g\(^{-1}\), and good capacity retention of 75% was observed after 5000 cycles at 15 A g\(^{-1}\). The outstanding performance of Co\(_3\)O\(_4\) NP@NC@CNTs is attributed to its unique structure, which can effectively accommodate the volume expansion of Co\(_3\)O\(_4\) NPs and improve electron/ion transportation in and among the active particles. The electrochemical kinetics investigation confirmed a faster charge transfer rate and easier redox reactions. To the best of our knowledge, this is the best electrochemical performance among other reported Co-based electrodes. These results confirm the structural superiority of this Co\(_3\)O\(_4\) NP@NC@CNTs electrode and would shed light the prospects for further designing other high performance LIB materials.

Associate Content

Supporting Information

The supporting information is available free of charge on the ASC Publications website.

SEM images of ZIF-67, Co NP@NC, Co\(_3\)O\(_4\) NP@NC@CNTs; XRD patterns of ZIF-67 and Co NP@NC; Raman curve for Co\(_3\)O\(_4\) NP@NC; TGA curve of Co\(_3\)O\(_4\) NP@NC; TEM images of Co\(_3\)O\(_4\) NP @NC; N\(_2\) isotherms of Co\(_3\)O\(_4\) NP@NC@CNTs and Co\(_3\)O\(_4\) NP@NC; Discharge/charge profiles of Co\(_3\)O\(_4\) NP@NC@CNTs and Co\(_3\)O\(_4\) NP@NC; Electrochemical comparison of the electrochemical performance reported in this work with other reports; Data for the Arrhenius fitting.

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REFERENCES


(5) Reddy, M. V.; Subba Rao, G. V.; Chowdari, B. V. Metal Oxides and Oxysalts as Anode...


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