

*Supporting information for*

**Electrospinning synthesis of  $\text{Co}_3\text{O}_4@\text{C}$  nanofibers as high-performance anode for sodium ion batteries**

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1. Thermogravimetric analysis (TGA) of  $\text{Co}_3\text{O}_4@\text{CNFs}$ ,  $\text{Co}_3\text{O}_4@\text{CNFs-2}$  and  $\text{Co}_3\text{O}_4@\text{CNFs-3}$

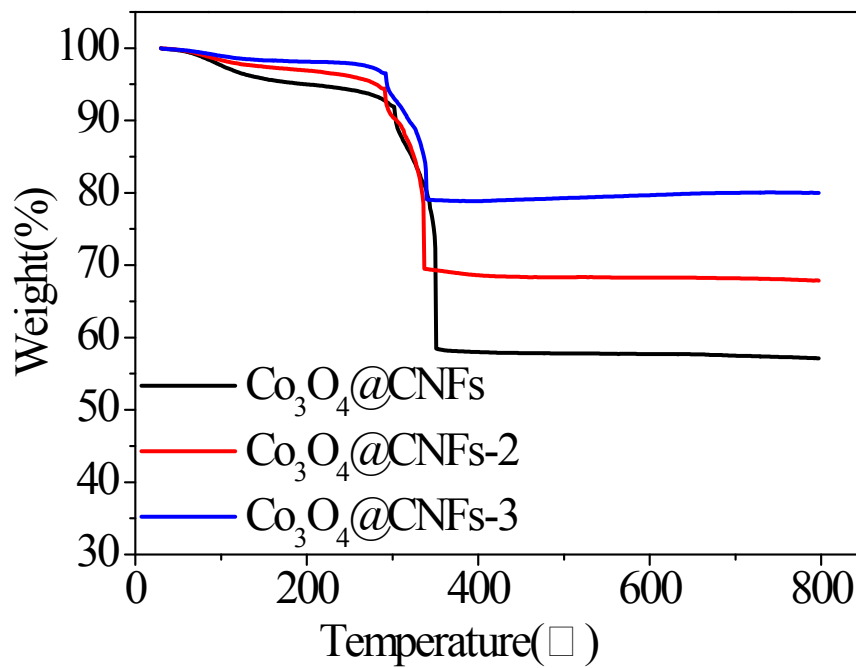


Fig. S1 TGA curves of  $\text{Co}_3\text{O}_4@\text{CNFs}$ ,  $\text{Co}_3\text{O}_4@\text{CNFs-2}$  and  $\text{Co}_3\text{O}_4@\text{CNFs-3}$  corresponding to the carbon contents of 41.2 wt %, 29.8 wt % and 18.4 wt %, respectively.

## 2. Nitrogen adsorption-desorption isotherm for CNFs

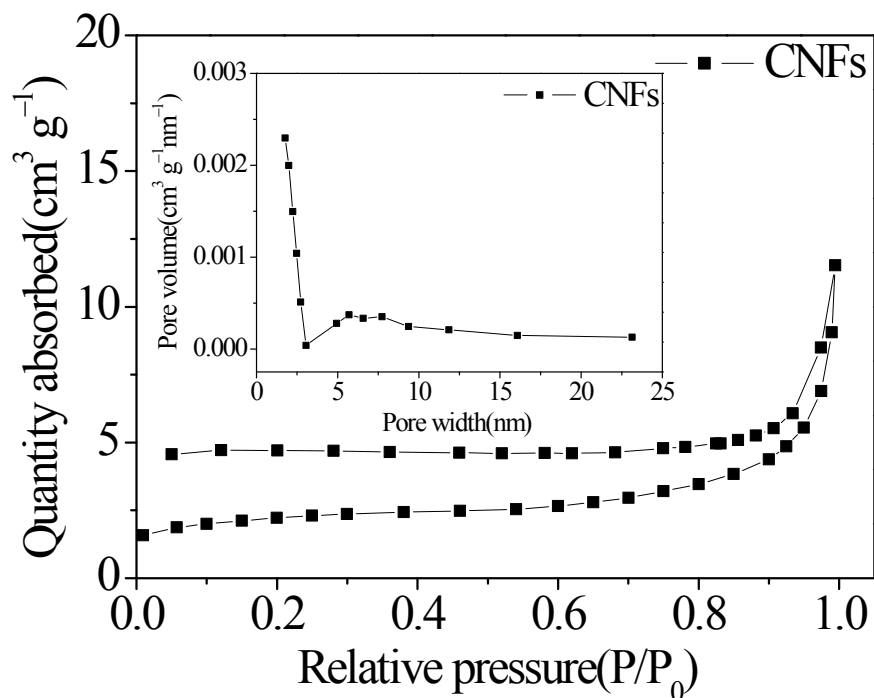


Fig. S2 Nitrogen adsorption-desorption isotherm for CNFs.

The specific surface area and pore size of CNFs are calculated to be  $7.80 \text{ m}^2 \text{ g}^{-1}$  and  $12.1 \text{ nm}$ .

## 3. Typical XPS spectra of the $\text{Co}_3\text{O}_4@\text{CNFs}$

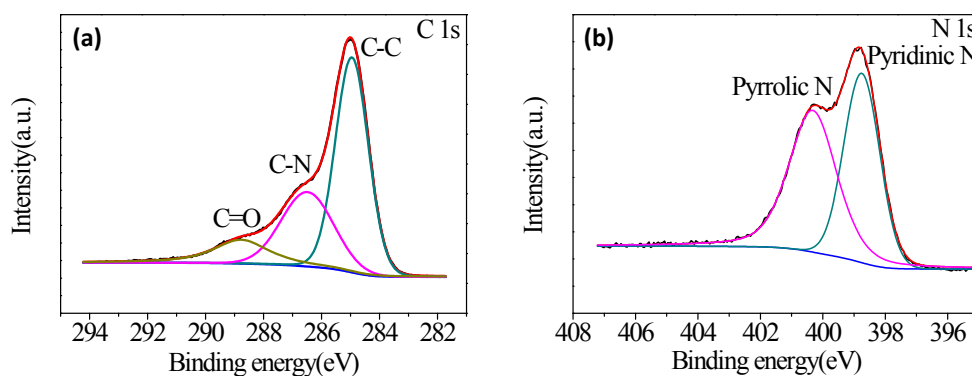


Fig. S3 Deconvoluted XPS spectra of (a) C 1s; (b) N 1s.

For high resolution scan of C 1s (see Fig. S3(a)), there exist three binding energies at 284.7, 286.2 and 288.5 eV, corresponding to C-C, C-N and C=O functional groups respectively by deconvoluted the spectrum. The N 1s (Fig. S3(b)) spectrum shows two kinds of N in the

composite : pyridine-like N (398.2 eV, an atom bonding with two carbon atoms), pyrrolic N (400.6 eV). The pyridine-like N can directly bond with metal atoms, exhibiting positive effects on the storage of  $\text{Na}^+$ . The C content is estimated to be 46.39 wt % by XPS elemental analysis which is in consistent with the TGA analysis showing a carbon content of 41.2 wt %.The discrepancy is due to the shallow penetration depth of X-ray photoelectrons, while the  $\text{Co}_3\text{O}_4$  nanoparticles are mostly embedded inside the CNFs.

#### 4. Surface morphology of $\text{Co}_3\text{O}_4$ NFs

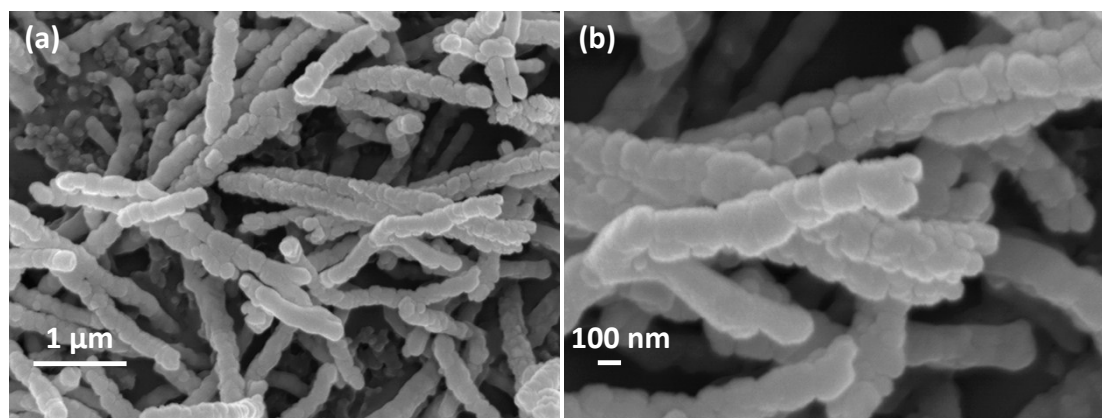


Fig. S4 SEM images of  $\text{Co}_3\text{O}_4$  NFs at different magnifications.

## 5. Electrochemical performances of $\text{Co}_3\text{O}_4$ NFs and CNFs

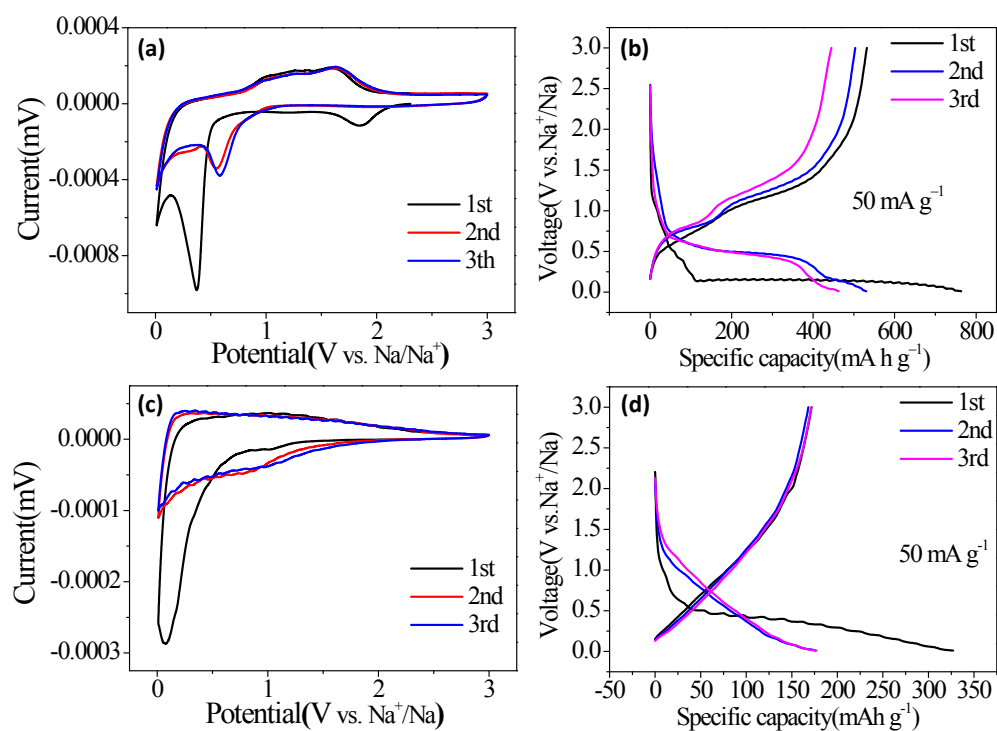


Fig. S5 Cyclic voltammograms (CVs) of (a)  $\text{Co}_3\text{O}_4$  NFs and (c) CNFs at a scan rate of  $0.1 \text{ mV s}^{-1}$  between 0.01-3.0 V for the first three cycles; Galvanostatic charge/discharge curves of (b)  $\text{Co}_3\text{O}_4$  NFs and (d) CNFs for the first three cycles between 0.01-3.0 V versus  $\text{Na}^+/\text{Na}$ .

## 6. Cycling performances of $\text{Co}_3\text{O}_4@\text{CNFs}$ treated at different temperature

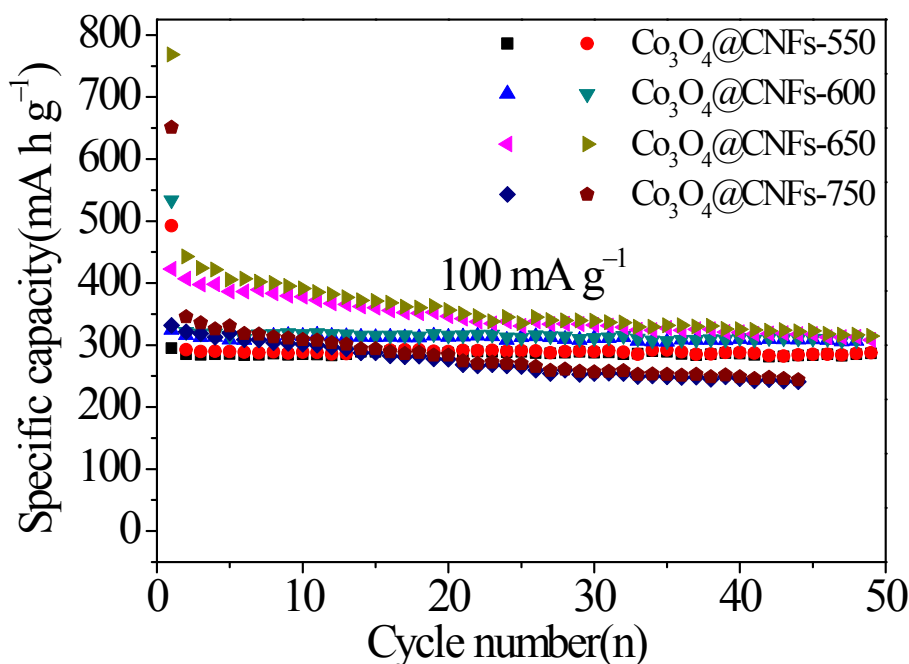


Fig. S6 Comparison of the cycling performance of  $\text{Co}_3\text{O}_4@\text{CNF}$ -550,  $\text{Co}_3\text{O}_4@\text{CNF}$ -600,  $\text{Co}_3\text{O}_4@\text{CNF}$ -650 and  $\text{Co}_3\text{O}_4@\text{CNF}$ -750 between 0.01-3 V versus  $\text{Na}^+/\text{Na}$  at a current density of  $100 \text{ mA g}^{-1}$ .

The cycling performance of  $\text{Co}_3\text{O}_4@\text{CNF}$ -550,  $\text{Co}_3\text{O}_4@\text{CNF}$ -600,  $\text{Co}_3\text{O}_4@\text{CNF}$ -650 and  $\text{Co}_3\text{O}_4@\text{CNF}$ -750 was carried out at a current density of  $100 \text{ mA g}^{-1}$  in the voltage range of 0.01-3.0 V (versus  $\text{Na}^+/\text{Na}$ ) up to 100 cycles, as shown in Fig S6. Compared with  $\text{Co}_3\text{O}_4@\text{CNF}$ -550,  $\text{Co}_3\text{O}_4@\text{CNF}$ -600 and  $\text{Co}_3\text{O}_4@\text{CNF}$ -750 with an initial discharge specific capacity of 492.6, 533.9 and 651.1  $\text{mA h g}^{-1}$  respectively,  $\text{Co}_3\text{O}_4@\text{CNF}$ -650 composite delivered much higher initial discharge specific capacity of 768.4  $\text{mA h g}^{-1}$ , which was very close to the theoretical specific capacity of  $\text{Co}_3\text{O}_4$  (889  $\text{mA h g}^{-1}$ ). However, the initial coulombic efficiency decreased with the increase of the carbonized temperature, which may be caused by the increase of the specific surface area and graphitization degree at higher carbonized temperature. After 50 cycles,  $\text{Co}_3\text{O}_4@\text{CNF}$ -550,  $\text{Co}_3\text{O}_4@\text{CNF}$ -600 and  $\text{Co}_3\text{O}_4@\text{CNF}$ -750 only displayed a specific capacity of 286.5, 306.9 and 241  $\text{mA h g}^{-1}$  respectively, while  $\text{Co}_3\text{O}_4@\text{CNF}$ -650 still remained a specific capacity of 312.1  $\text{mA h g}^{-1}$ , exhibiting much higher specific capacity and better cycling stability.

7. The comparison of the SEM images of  $\text{Co}_3\text{O}_4@\text{CNFs}$  and  $\text{Co}_3\text{O}_4$  NFs before and after cycling

The electrodes of  $\text{Co}_3\text{O}_4@\text{CNFs}$  and  $\text{Co}_3\text{O}_4$  NFs after cycling 50 cycles were first taken out from the assembled cells in an Ar-filled glovebox, and then soaked in propylene carbonate (PC) solvent for several days to wash the electrolyte salts ( $\text{NaClO}_4$ ) and fluoroethylene carbonate (FEC) additive. Finally, the washed electrodes were dried in an electrical oven to remove the PC solvent. Before SEM testing, the as-prepared electrodes were kept in the glovebox and sealed well in a tube.

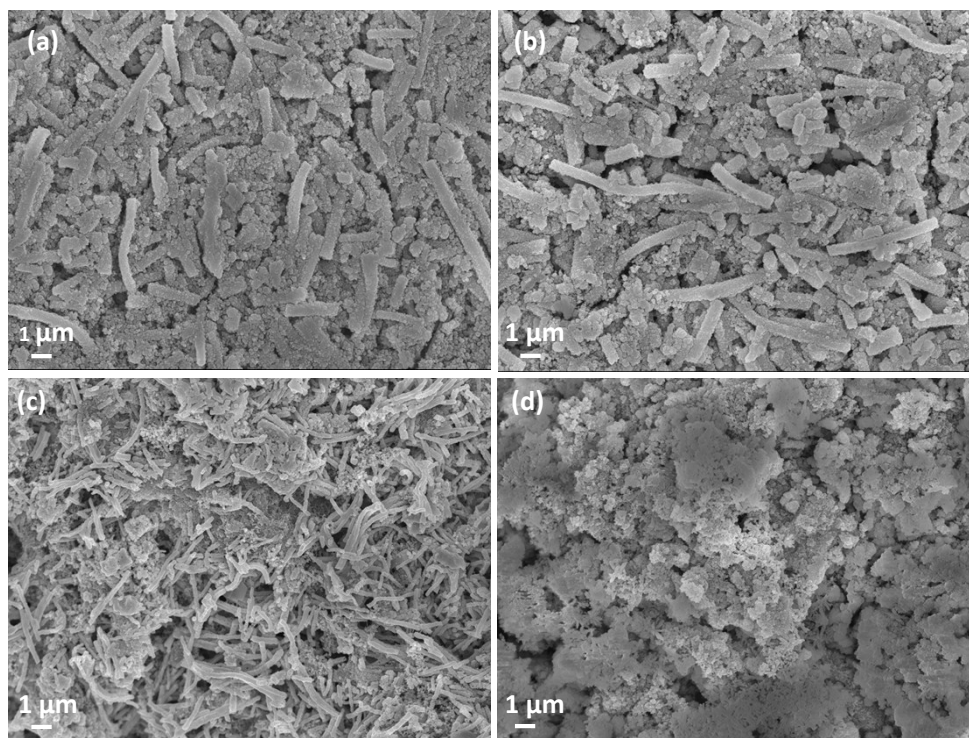


Fig. S7 (a,b) SEM images of  $\text{Co}_3\text{O}_4@\text{CNFs}$  before and after cycling 50 cycles at  $50 \text{ mA g}^{-1}$ . (c,d) SEM images of  $\text{Co}_3\text{O}_4$  NFs before and after 50 cycles at  $50 \text{ mA g}^{-1}$ .

8. Raw and fitting electrochemical impedance spectra (EIS) of the of the  $\text{Co}_3\text{O}_4@\text{CNFs}$  and  $\text{Co}_3\text{O}_4$  NFs

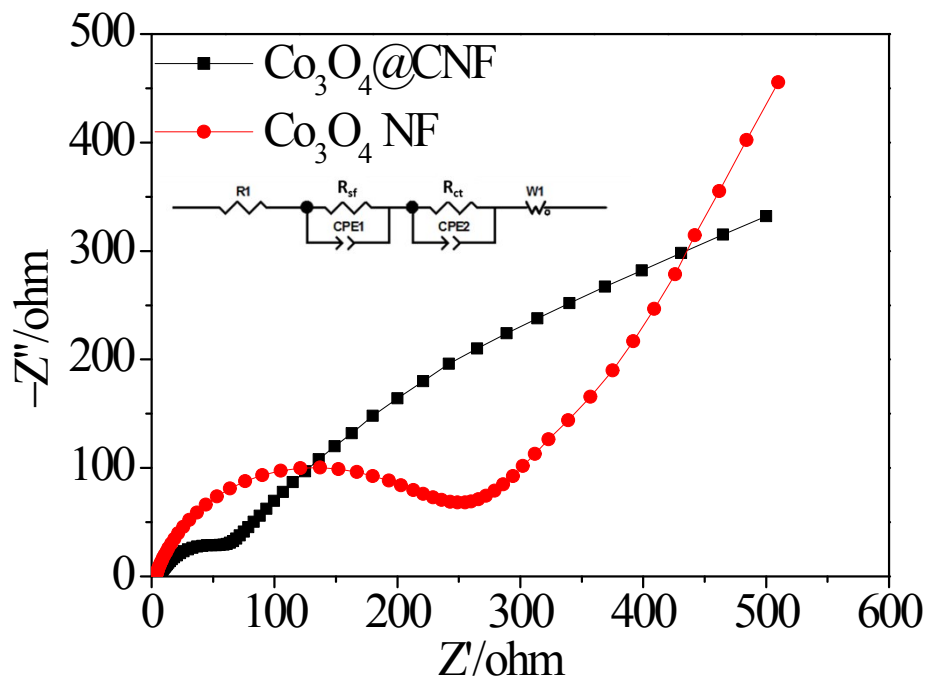


Fig. S8 Nyquist plots of the  $\text{Co}_3\text{O}_4@\text{CNF}$  and  $\text{Co}_3\text{O}_4$  NF electrodes after 50 cycles and the equivalent circuit (inset) to fit the EIS spectra.

Table. S1 Impedance parameters of  $\text{Co}_3\text{O}_4@\text{CNF}$  composite and pure  $\text{Co}_3\text{O}_4$  NF electrodes.

Sample	$R_e$	$R_{sf}$	$R_{ct}$
$\text{Co}_3\text{O}_4@\text{CNF}$	4.5 $\Omega$	2.1 $\Omega$	41.4 $\Omega$
$\text{Co}_3\text{O}_4$ NF	3.6 $\Omega$	3.4 $\Omega$	223.4 $\Omega$

The EIS spectra of  $\text{Co}_3\text{O}_4@\text{CNFs}$  and  $\text{Co}_3\text{O}_4$  NFs consist of two overlapping semicircles in the high and medium frequency range and a sloping straight line in the low frequency range. The EIS data was fitted by an equivalent circuit as shown in Fig. S8 (inset).  $R_e$  is the ohmic resistance, which stands for the total resistance of the electrolyte, the separator and the electrical contact. The semicircle in the high frequency region reflects the migration of  $\text{Na}^+$  through the SEI film ( $R_{sf}$ ) and the charge transfer resistance ( $R_{ct}$ ). The inclined line in the low frequency range reflects the diffusion properties of  $\text{Na}^+$  in solid materials ( $Z_w$ ). The fitted results were summarized in Table.



S1. It can be observed that  $R_{sf}$  and  $R_{ct}$  of  $\text{Co}_3\text{O}_4@\text{CNF}$  were  $2.1 \Omega$  and  $41.4 \Omega$ , respectively, which were different from those of  $\text{Co}_3\text{O}_4 \text{ NF}$  ( $3.4$  and  $223.4 \Omega$ ).