Supporting Information

Low-Temperature Metal-Catalyzed Synthesis of Metal Oxide Nanoparticles Encapsulated and Nitrogen-doped Carbon Nanotubes from Carbon Nitride as Anodic Materials of High-Performance Lithium-Ion Batteries

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Experimental Section

Preparation of Samples.

The synthesis of C₃N₄: 10 g melamine was pressed into a pellet under a pressure of 20 MPa. The pellet was transferred to a semiclosed quartz boat and calcined at 600 °C for 0.5 h in N_2 atmosphere. Then the obtained yellow powder was collected as the carbon and nitrogen precursor for the preparation of metal@NCNT.

The in situ synthesis of Co@NCNT and Ni@NCNT arrays: 2 g $Co(CH_3COO)_2 \cdot 4H_2O$ or $Ni(CH_3COO)_2 \cdot 4H_2O$ and 5 g C_3N_4 were added to 5 ml aqueous solution under tempestuously stirring to form a yellow slurry. Then, the colloidal compounds were milled continually to form a yellow paste, following the evaporation of water. The obtained yellow paste was dried at 80 °C for 24 h and manually ground into powder. The powder was transferred to a semiclosed quartz boat and heated at 350 °C for 1 h at a heating rate of 2 °C min⁻¹ in a tubular furnace under N_2 flow, and the temperature was increased to 700 °C at 2 °C min⁻¹ and kept at 700 °C for 3 h, followed by cooling to room temperature naturally.

The in situ synthesis of Co₃O₄@NCNT and NiO@NCNT arrays: The obtained Co@NCNT and Ni@NCNT powder was calcined in a muffle furnace in air at 400 °C for 0.5 h with a heating rate of 10 °C min⁻¹, and the final product was obtained.

The synthesis of Co₃O₄/CB: 2 g $Co(CH_3COO)_2 \cdot 4H_2O$ and 0.5 g carbon black was dispersed in 3 ml deionized water and ground by mortar and pestle to form a slurry. Then the slurry was dried at 80 °C in oven overnight. The obtained powder was transferred to a quartz boat and covered by a quartz cap. Then heat treated at 400 °C for 1 h in air to form Co₃O₄/CB.

Material Characterization

The crystalline structure of the products was characterized by X-ray diffraction (XRD) on a Rigaku SmartLab9 powder diffractometer equipped with Cu K_α radiation (λ = 1.541 Å). Thermogravimetric analysis (TGA) was performed on a TA SDT Q600 analyser in air with a heating rate of 10 K min^{-1}. The morphology of the products was observed by field emission scanning electron microscopy (FE-SEM) on a ZEISS SUPRA 55 microscope and transmission electron microscopy (TEM) on a Tecnai G2 F20 microscope. X-ray photoelectron spectroscopy (XPS) was conducted using a Kratos Axis Ultra DLD (delay line detector) spectrometer equipped with a monochromatic Al K_α X-ray source (1486.6 eV). Raman spectra were collected on a Renishaw-1000 spectrometer by exciting a 514.5 nm Ar ion laser. N_2 adsorption-desorption isotherms were recorded at 77 K on a Quantachrome NOVA 2000e sorption analyzer. Optical absorption spectroscopy was performed in the 300-700 nm range in 1 nm steps on an ultraviolet-visible-near-infrared, double beam spectrophotometer (America PerkinElmer Lambda 950).

Electrochemical Characterization

Co_3O_4@NCNT, NiO@NCNT or Co_3O_4/CB and polyvinylidene fluoride (PVDF) binder in a weight ratio of 9 : 1 were mixed in N-methylpyrrolidone (NMP) and stirred for 24 h to make a slurry. The slurry was then spread on a Cu foil (13 mm in diameter, 0.3 mm in thickness) with a surface density of 1.0 mg cm^{-2} and dried at 120 °C for 24 h to fabricate the working electrodes in vacuum. Lithium foil was used as both the reference electrode and the counter electrode (13 mm in diameter, 0.5 mm in thickness). 1.0 M LiPF$_6$ in a 1:1 (*v/v*) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) was employed as the electrolyte. Celgard 2300 membrane (25 μm-thick polyethylene) was adopted as a separator. The assembly of CR2032-type coin cells was conducted in a high-purity Ar filled glovebox. Galvanostatic cycling was performed between 0.01 and 3 V *vs* Li$^+$/Li at various C rates on a Land Battery Tester (Wuhan, China), where 1 C corresponds to 1000 mA g^{-1}. Cyclic voltammetry (CV) was conducted between 0.01 and 3 V at 0.1 mV s^{-1} using a CHI660E electrochemical

workstation. Electrochemical impedance spectroscopy (EIS) was performed on the same electrochemical system over the frequency range from 100 kHz to 100 mHz with a perturbation voltage of 5 mV. All of the electrochemical measurements were performed at 25 °C in an ambient atmosphere.
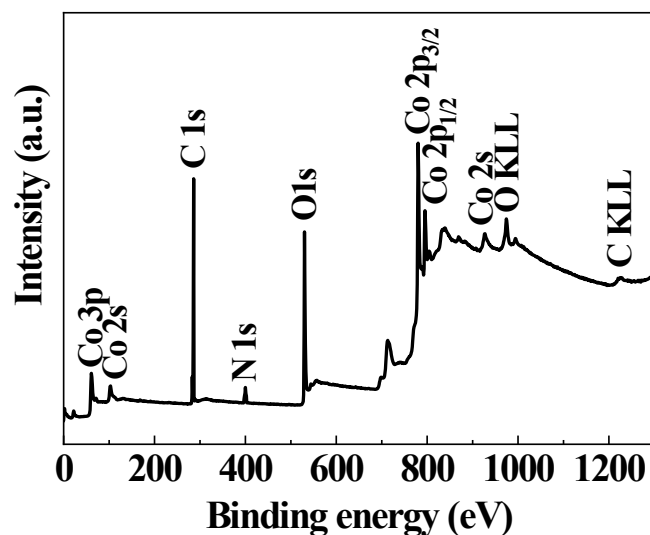
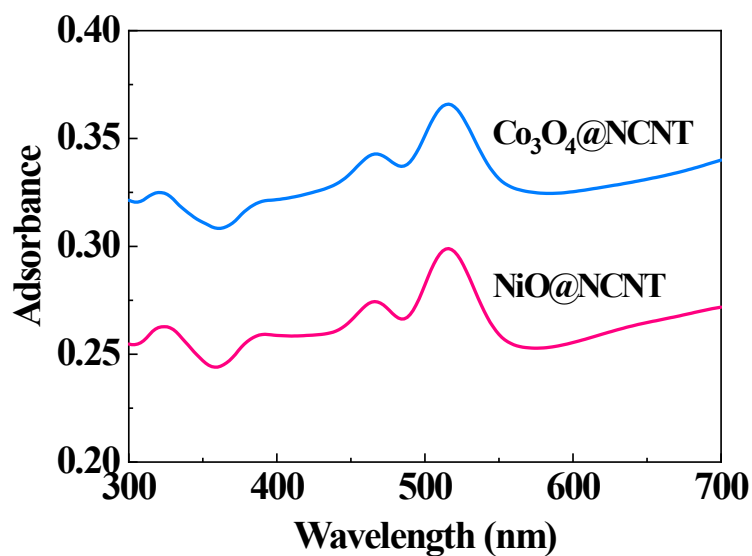

Fig. S1 XPS survey spectrum of Co_3O_4@NCNT hybrid.

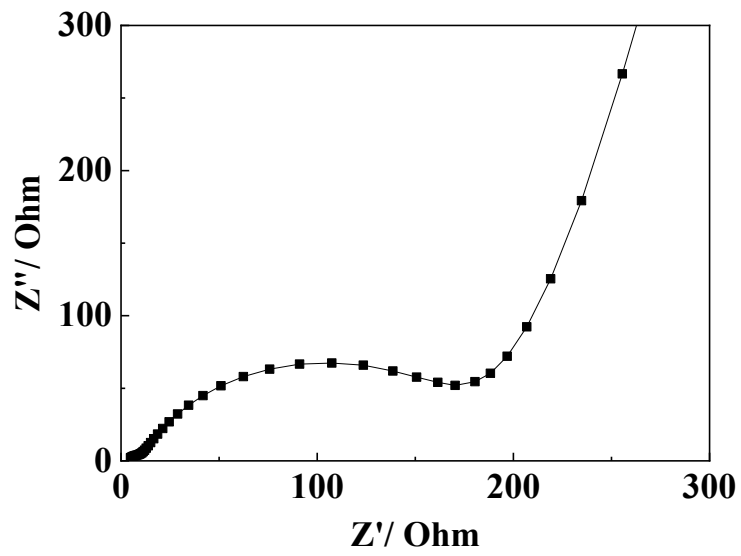**Fig. S2** Absorption spectrum of Co_3O_4@NCNT and NiO@NCNT hybrids.
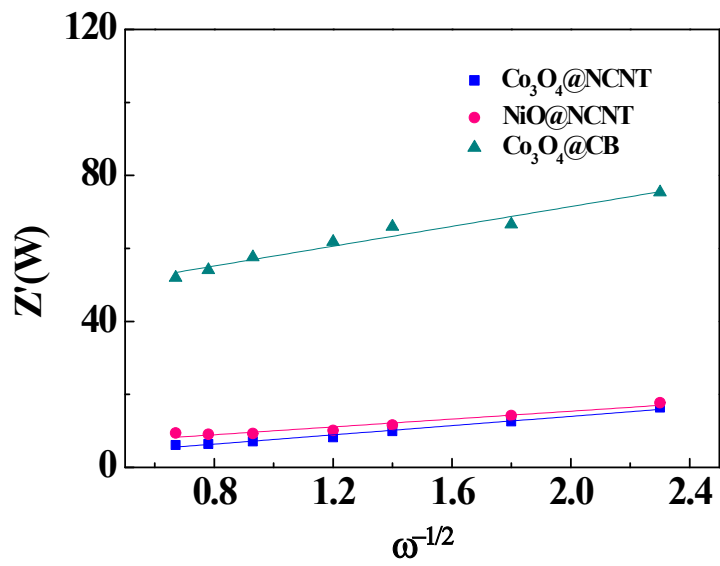
Fig. S3 Nyquist plot of Co_3O_4/CB.

Fig. S4 The relationship between Z' and $\omega^{-1/2}$ in the low-frequency region for LiFePO4@C@CNT anodes.

To further confirm the effect of one-dimensional nanostructure on the electrolyte ions diffusion, the measurement of electrolyte ions diffusion coefficients (D_{Li^+}) based on *eq*. 1 are very necessary.[1]

$$D = \frac{R^2T^2}{2A^2n^4F^4C^2\sigma^2}$$

(1)

where D is the diffusion coefficient of Li$^+$, R is the gas constant, T is the absolute temperature, A is the surface area of the anode (0.15 m^2), n is the number of electrons involved in the redox reaction of $Co^{3+}/Co^{2+}/Co$ at the electrode, F is the Faraday constant, C is the concentration of Li$^+$ (7.69 $\times$ 10^{-3} mol cm^{-3}), σ is the Warburg factor. According to the *eq*. 2, the σ varies negatively with D, suggesting that the lower σ corresponds to the higher-rate ions diffusion in the electrode. The σ can be directly derived from the slope of straight line in the Nyquist plots based on eq. 2.[2] Fig. S4 presents the relationship between Z′ and reciprocal square root

$$Z' = R_D + R_L + \sigma\omega^{-1/2}$$

(2)

of angular frequency ($\omega^{-1/2}$) in the low-frequency region, in which the slope of straight line represents σ. The σ firstly slightly decreases from Co_3O_4@NCNT (6.3) to NiO@NCNT (5.4) and then largely increases to Co_3O_4@CB (13.6), demonstrating the D_{Li^+} of Co_3O_4@NCNT and NiO@NCNT was effectively enhanced in the one-dimensional nanostructure.

1. B. Wang, Z. Zhang, Y. Ning, X. Li, T. Ruan, F. Wang, D. Wang and Y. Zhou, *Energy Technology*, 2020, **8**, 2000171.
2. D. Saikia, J. R. Deka, C.-J. Chou, C.-H. Lin, Y.-C. Yang and H.-M. Kao, *ACS Applied Energy Materials*, 2019, **2**, 1121-1133.