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Supporting Information for

Co_3O_4 Nanoparticles Embedded Carbonaceous Fibre: Nanoconfinement Effect on Enhanced Lithium-Ion Storage

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Experimental Section

Materials

Regenerated cellulose was obtained from Shandong Helon Co., Ltd. (Shandong, China). Sodium sulfate anhydrous [Na_2SO_4], sodium hydroxide [NaOH], ethanol [CH_3CH_2OH], chloroacetic acid [$ClCH_2COOH$], and cobalt chloride hexahydrate [$CoCl_2·6H_2O$] were purchased from Sinopharm Chemical Reagent (Shanghai, China) and used without further purification. Sulfuric acid [H_2SO_4] was purchased from the Shuangshuang Chemistry Company (Yantai, China).

Preparation of Co_3O_4/CF-X

The RC solution was filtered, and then extruded from a spinneret into a coagulating bath containing 8 wt% H_2SO_4/20 wt% Na_2SO_4 aqueous solution to form RCFs, and then washed with distilled water. The RCFs were soaked and vibrated in 5 wt% sodium hydroxide-ethanol solution at 60 °C for 4 h, then chloroacetic acid was added to the solution and vibrated at 60 °C for 4 h, so that the cellulose were modified. The processes of the reactions can be described as follows:

$$Cellulose\text{-}OH + NaOH \rightarrow Cellulose\text{-}ONa + H_2O$$
$$Cellulose\text{-}ONa + ClCH_2COOH \xrightarrow{NaOH} Cellulose\text{-}OCH_2COONa + NaCl + H_2O$$

The obtained samples were washed with ethanol and dried, and then soaked and vibrated in 5 wt% cobalt chloride ethanol solution at 60 °C for 12 h, giving rise to Co-RCFs. The process of the reaction can be described as follow:

$$2Cellulose\text{-}OCH_2COONa + CoCl_2 \rightarrow$$
$$Cellulose\text{-}OCH_2COO\text{-}Co\text{-}OOCH_2O\text{-}Cellulose{+}2NaCl$$

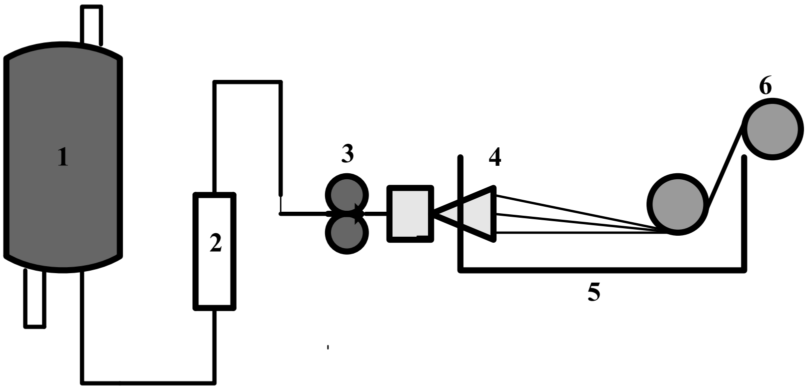
The Co-RCFs were carbonized at 800 °C for 1 h under N_2 atmosphere and subsequent oxidation in air to form the Co_3O_4/CF-X. The precursors oxidized with a time of 30, 60, and 90 min in air at 400 °C were noted as Co_3O_4/CF-30, Co_3O_4/CF-60, and Co_3O_4/CF-90, respectively.

Characterizations

The phase structures were characterized with X-ray diffraction (XRD, DX2700, China) operating with Cu Kα radiation (l = 1.5418 Å) at a scan rate (2θ) of 2° min^{-1} with the accelerating voltage of 40 kV and the applied current of 30 mA, ranging from 5 to 90°. The samples were analyzed by Fourier Transformed Infrared spectroscopy (FTIR; Nicolet 5700, Thermo Electron Co., USA) in the wavelength range of 500-4000 cm^{-1}. Specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method from the data in a relative pressure (P/P_0) range between 0.05 and 0.20, pore size distribution plots were derived from the adsorption branch of the isotherms based on the BJH model. The morphology was investigated by field emission scanning electron microscopy (SEM; JSM-7001F, JEOL, Tokyo, Japan) with energy dispersive X-ray spectroscopy (EDS). TEM images were obtained using a FEI Tecnai 20 TEM with an accelerating voltage of 200 kV. Thermogravimetric analysis (TGA) measurement was carried out on an EXSTAR TG/DTA 6300 instrument (Seiko Instruments, Japan) with a heating rate of 5 °C min^{-1} in air.

Electrochemical Measurements

The Co_3O_4/CF-X was mixed with acetylene black and poly (vinylidene fluoride) (PVDF) at a weight ratio of 8:1:1 in N-methyl-2-pyrrolidone (NMP) solvent to form the slurry. Then, the resultant slurry was uniformly pasted on Cu foil substrate. The prepared electrode sheet was dried in a vacuum oven at 100 °C for 10 h and then pressed. The electrolyte consisted of a solution of 1 M $LiPF_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC) (1:1:1, in wt%). CR2016-type coin cells were assembled in a glove box for electrochemical characterization. Lithium metal foil was used as the counter and reference electrode. The discharge and charge measurements were conducted using a cell testing instrument (LAND CT2001A) over the potential range from 0.01 to 3.00 V. Cyclic voltammetry (CV) (0.01 to 3.0 V, 0.1 mV s^{-1}) was performed using an CHI-760 electrochemical workstation.



1. Spinning solution tank of regenerate cellulose solution
2. Polypropylene filter of 10 µm 3. Metering pump 4. Spinneret
5. Coagulation bath of 8 wt % H_2SO_4/20 wt % Na_2SO_4 aqueous solution
6. Filament roller

Fig. S1 Wet spinning process for the preparation of RCFs.

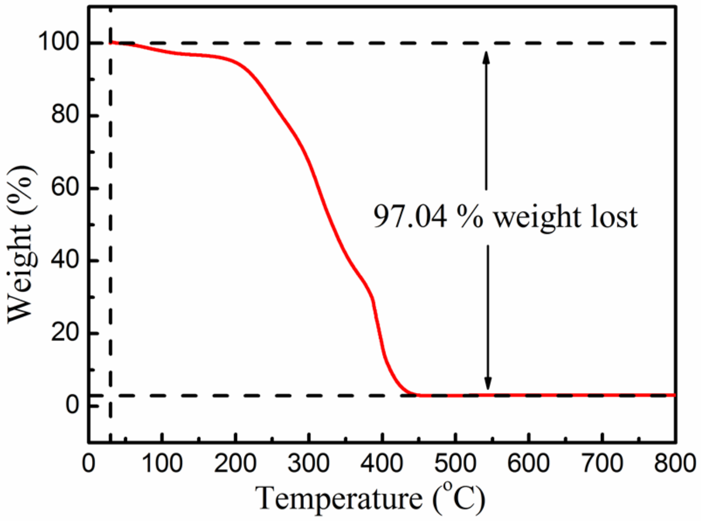


Fig. S2 The TGA curve of the Co-RCFs in air.

TGA measurement was used to determine the content of Co species in the Co-RCFs. The Co-RCFs were heated to 800°C in air. The whole process of thermal decompositions for the Co-RCFs is the result of decomposition of cellulose, and the residue is Co_3O_4. The content of residual Co_3O_4 is 2.96 wt%. Therefore, the weight percentage of Co species in Co-RCFs is about 2.17 wt%

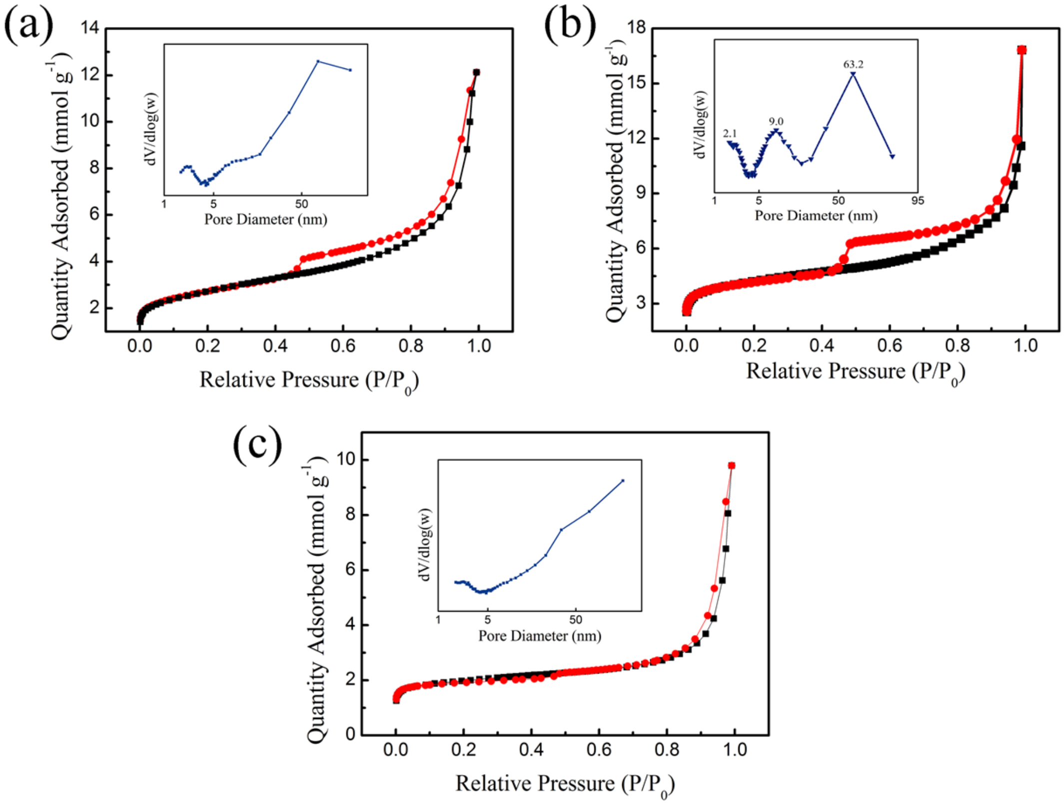


Fig. S3 Nitrogen adsorption-desorption isotherm and corresponding pore size distribution curve (inset) for (a) Co_3O_4/CF-30, (b) Co_3O_4/CF-60, and (c) Co_3O_4/CF-90.

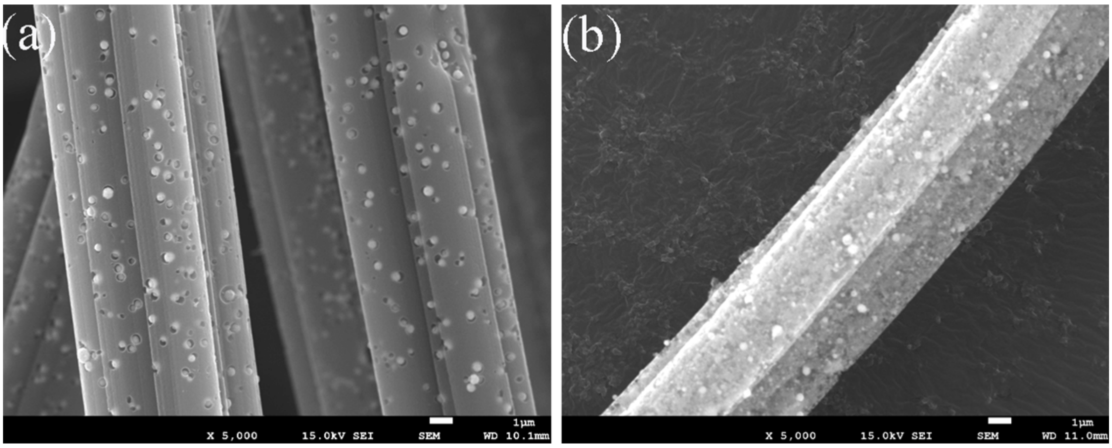


Fig. S4 SEM images of (a) Co_3O_4/CF-30, (b) Co_3O_4/CF-90

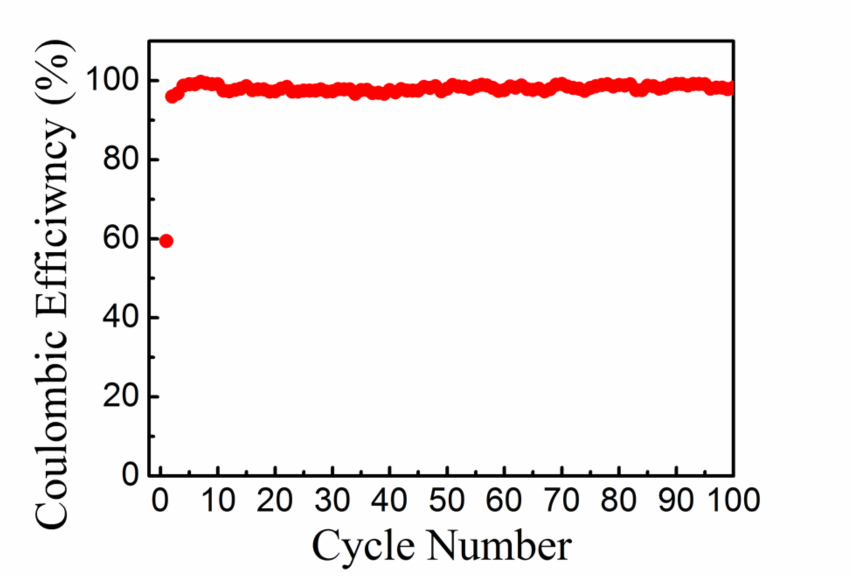


Fig. S5 The Coulombic sfficiency of Co_3O_4/CF-60 at a current density of 89 mA g^{-1}.

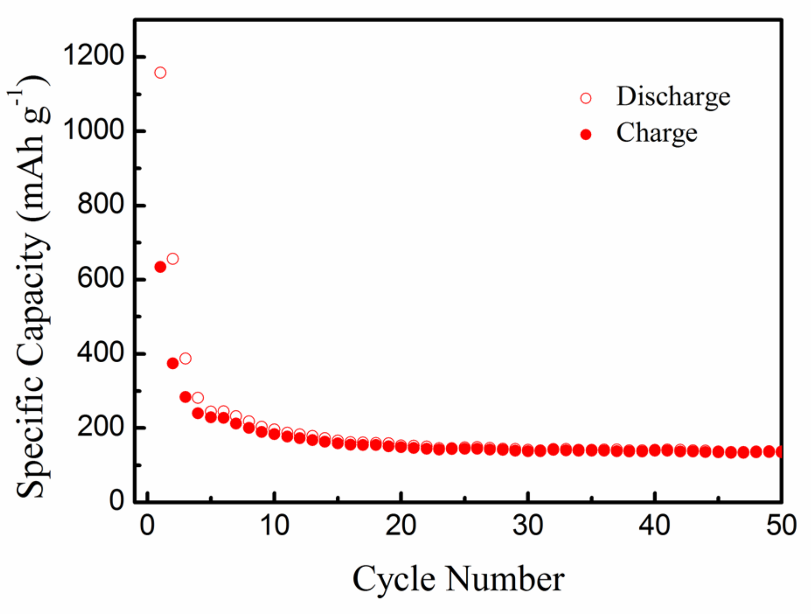


Fig. S6 The cycling performance of commercial Co_3O_4 at 89 mAh g^{-1}.

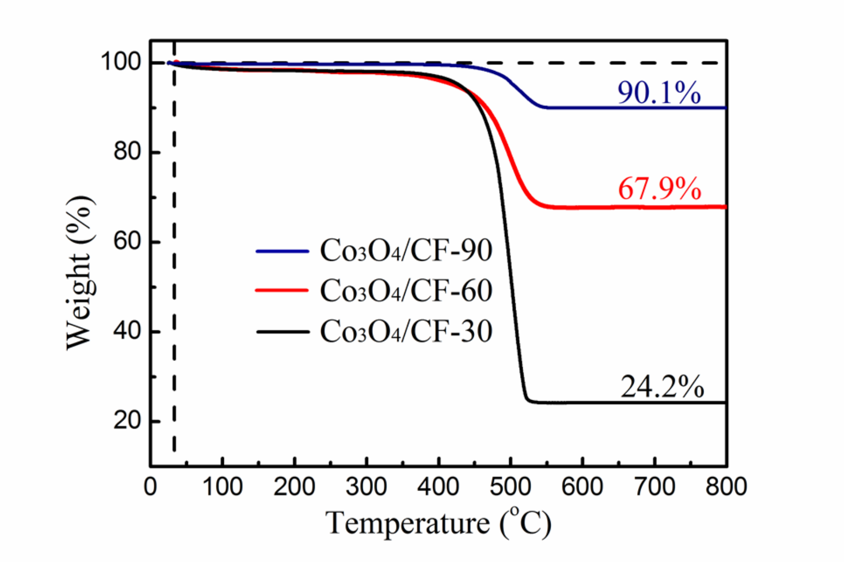


Fig. S7 The TGA curves of the Co_3O_4/CF-30, Co_3O_4/CF-60, and Co_3O_4/CF-90 in air.

TGA measurement shows the thermal decomposition of Co_3O_4/CF-x electrodes with a heating rate of 5 °C min^{-1} in air (Fig. S7). The whole process of thermal decompositions for all the samples is the result of decomposition of carbon, and the residue is Co_3O_4. The contents of carbon in Co_3O_4/CF-30 Co_3O_4/CF-60, and Co_3O_4/CF-90 are 75.8 wt%, 32.1wt%, and 9.9 wt%, respectively.

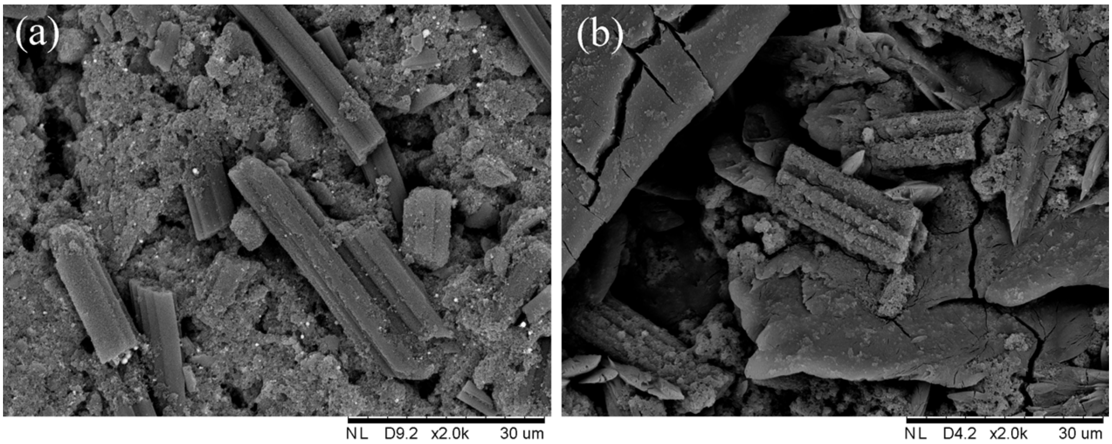


Fig. S8 The SEM images of Co_3O_4/CF-60 electrode (a) before galvanostatic charge-discharge cycle and (b) after 100 galvanostatic charge-discharge cycles.

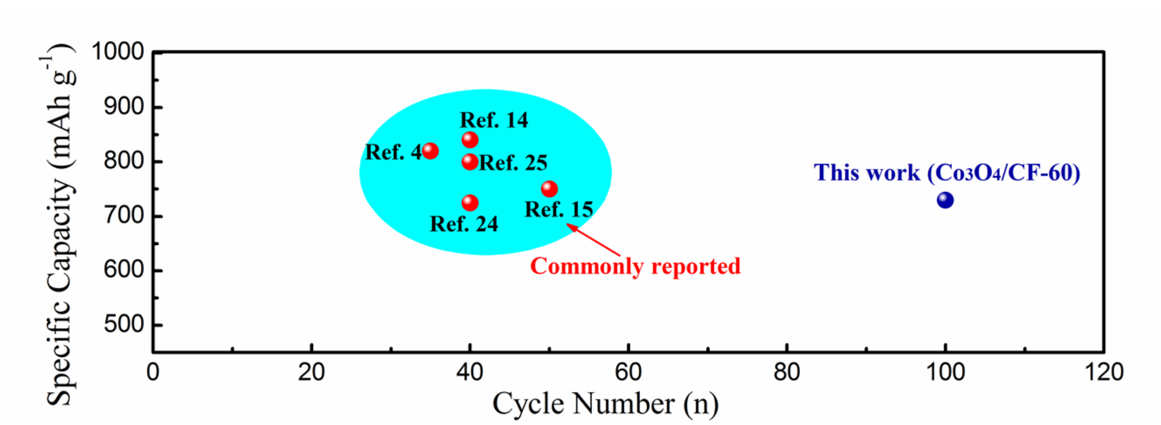


Fig. S9 Comparision of specific capacity and cycle life between Co_3O_4/CF-60 and recently reported high-performance Co_3O_4-based electrodes.