Electronic Supporting Information

A Facile Annealing Strategy Achieving In-situ Controllable Cu_2O Nanoparticles Decorated Copper Foil as Current Collector for Stable Lithium Metal Anode

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Experimental Procedures

Synthesis of CF@CNP

Copper oxide nanoparticles decorated copper foil (CF@CNP) was prepared by a vapor phase crystallization method in atmosphere environment. Typically, a copper foil (4×4 cm^2) was rinsed with absolute ethanol under ultrasonication for 15 min to purify the surface. After dried at 75 ºC in vacuum for 2h, the purified copper foil was pasted on a porcelain combustion boat and heated at 300 ºC in air for a certain amount of time, then cooled down to room temperature. According to the different heating time (30 or 60 min), the as-prepared current collectors were named as CF@CNP–30 and CF@CNP–60, respectively.

Characterizations

The X-ray diffraction (XRD) was tested with a Bruker D8 X-ray diffractometer (Cu Kα radiation, the wavelength of 1.5406 Å). The morphologies of the as-prepared CF@CNP and lithium dendrites were observed by scanning electron microscopy (SEM, Nova NanoSEM 230). X-ray photoelectron spectroscopy (XPS) measurements were performed on a K-Alpha1063 spectrometer with a monochromatic Al Kα radiation at 6 mA and 12 kV. Thermogravimetric analyses (TGA) are carried out in air with an STA 449 C thermoanalyzer at a heating rate of 5 °C min^{-1} from 25 to 1000 °C in air. Raman spectra were obtained using a LabRam HR800 spectrometer with an excitation wavelength of 633 nm.

Electrochemical measurements

The electrochemical lithium plating/stripping performance was tested in CR2016 coin-type cells with the as-prepared current collectors as the work electrodes, lithium foils as both the counter and reference electrodes and Celgard membranes K2045 as the separators. A solution containing 1 M bis (trifluoromethane) sulfonamide lithium salt (LiTFSI) in a mixture of 1, 3-dioxolane (DOL) and 1, 2-dimethoxyethane (DME) (v/v, 1:1) with 1 wt% $LiNO_3$ was used as electrolyte. The galvanostatic charge/discharge tests were performed using a Neware CT-3008W battery testing system. The assembled cells were first activated by three discharge-charge cycles between 0.01 and 1 V at 0.05 mA cm^{-2}. The lithium plating/stripping cycling stability measurement was performed using the galvanostatic discharge process with a specific capacity of 1 mAh cm^{-2} at 1 mA cm^{-2} for the lithium plating and the galvanostatic charge process with a cut-off potential of 1 V (vs Li^{+}/Li) at 1 mA cm^{-2} for the lithium stripping. A CHI660D electrochemical workstation was employed for electrochemical impedance spectroscopy (EIS) with a frequency range from 10^{5} to 10^{-2} Hz and cyclic voltammogram (CV) measurement at a scan rate of 0.2 mV s^{-1} between −0.1 and 1 V. For symmetric test, 4 mAh cm^{-2} of lithium was first plated on CF and CF@CNP at 1 mA cm^{-2}. Then the obtained CF and CF@CNP based lithium anodes (CF@Li and CF@CNP@Li) were extracted from the cell and two identical anodes were reassembled into symmetric batteries. The measurement was performed at 1 mA cm^{-2} with the capacity of 1 mAh cm^{-2}. The commercial $LiFePO_4$ cathode was employed for the full cell test. The cathode electrode was prepared by mixing $LiFePO_4$, acetylene black and polyvinylidene fluoride (PVDF) in a weight ratio of 8:1:1. The average mass loading of the active material was about 2 mg cm^{-2}. The CF@Li or CF@CNP@Li anode was used as the reference and counter electrode. The electrolyte was a solution containing 1 M $LiPF_6$ in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) with a volume ratio of 1:1. Before assembling the full cell, the as-prepared lithium anodes (CF@Li and CF@CNP@Li) extracted from the half-cell were first washed by DEC and dried up in glovebox. The full cells were cycled between 2.5 and 3.8 V at different current densities from 0.2 C to 5 C (1C = 170 mA g^{-1}).

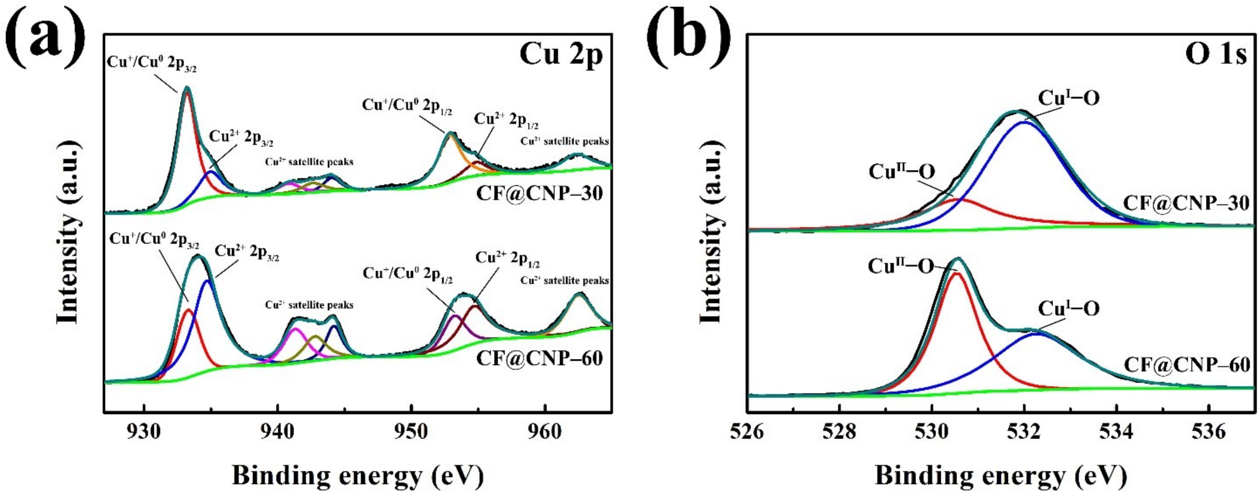

Fig. S1 (a) Cu 2p and (b) O 1s XPS spectrum of CF@CNP–30 and CF@CNP–60.

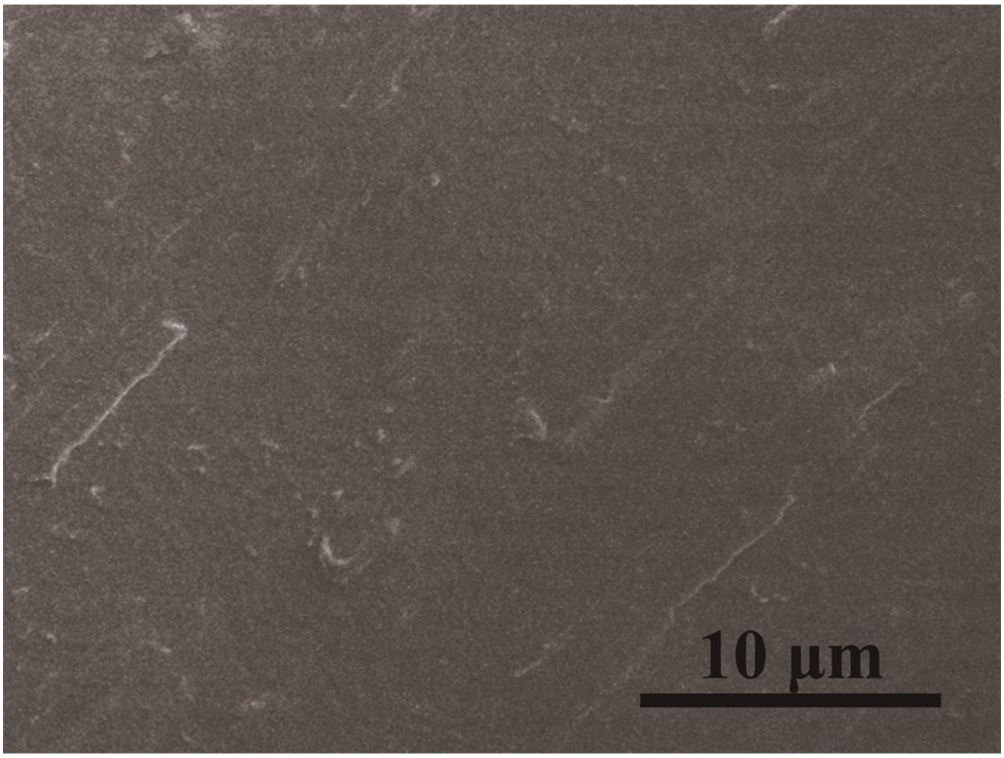

Fig. S2. SEM image of CF.

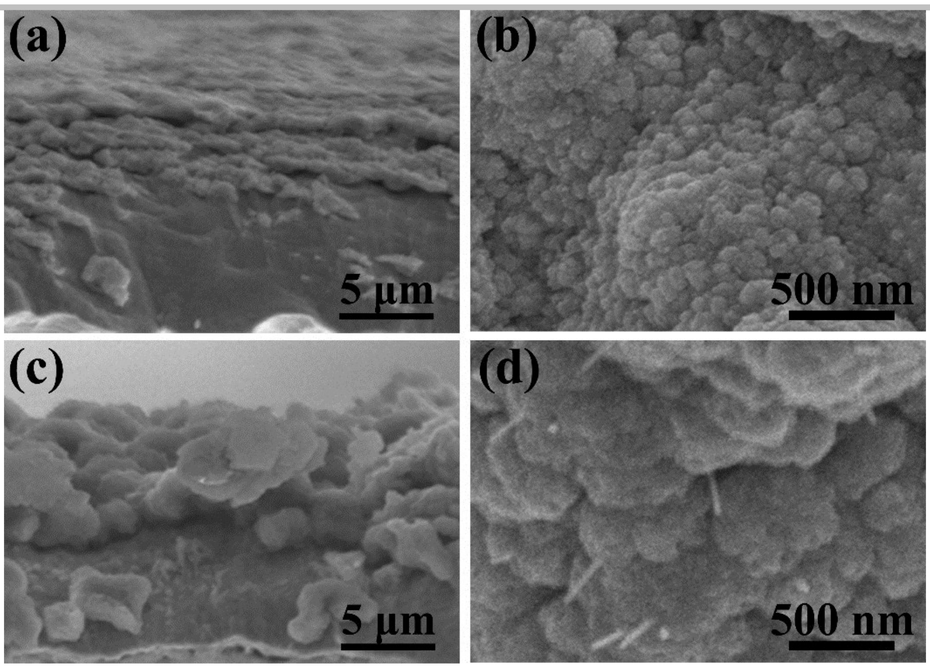

Fig. S3 SEM images of CF@CNP–30 (a, b) and CF@CNP–60 (c, d).

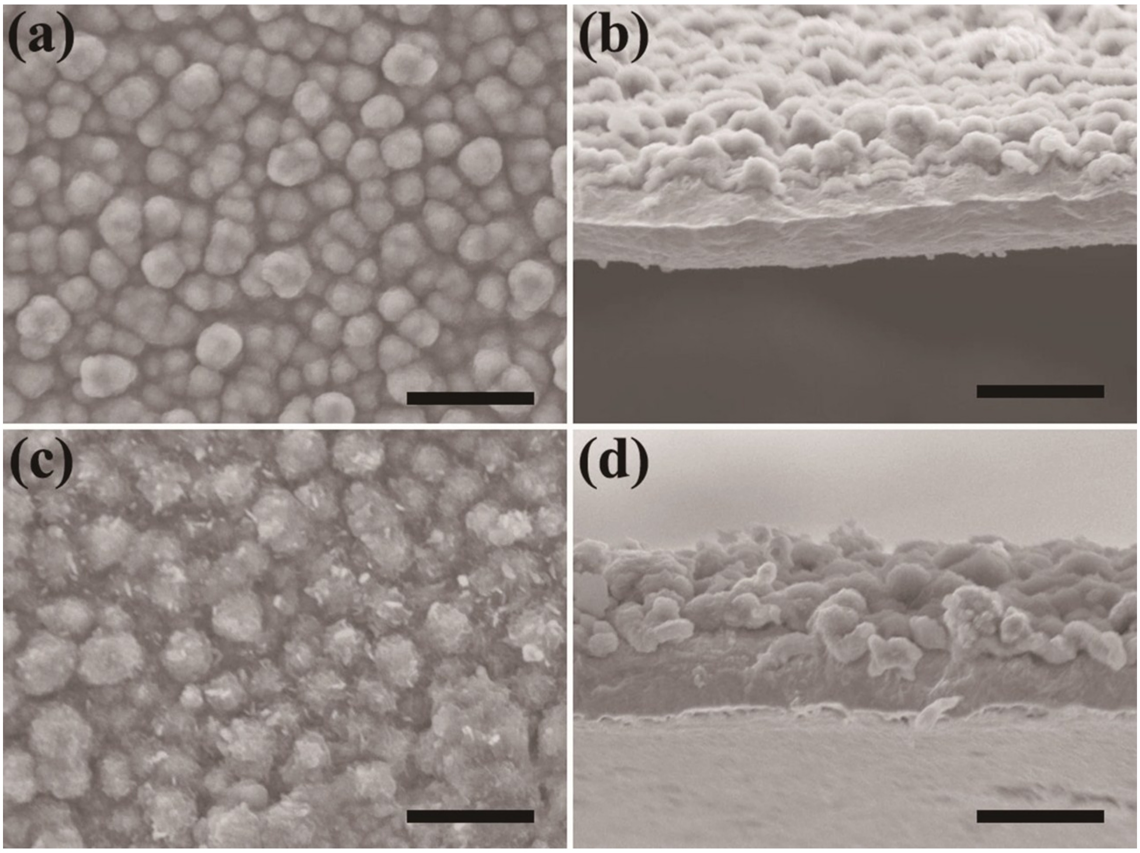

Fig. S4. SEM images of CF@CNP–30 (a, b) and CF@CNP–60 (c, d) after activation process. Scale bars, 15 μm.

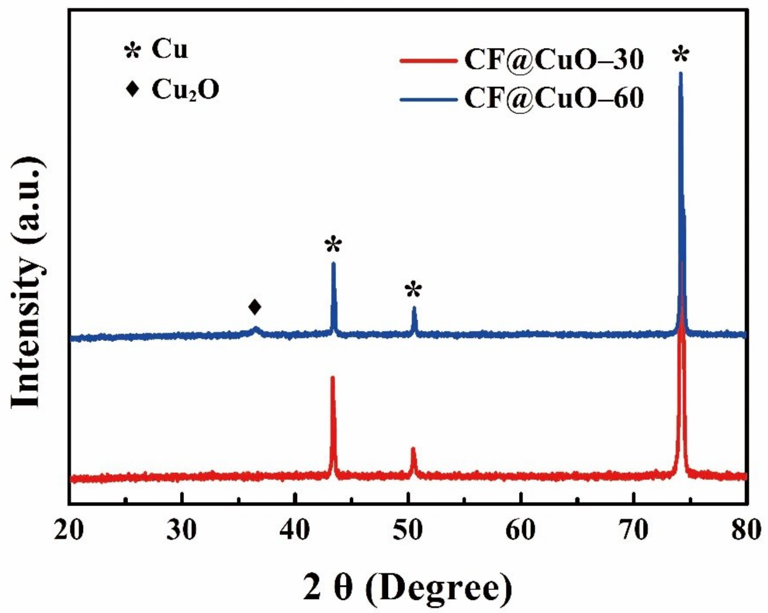

Fig. S5. XRD patterns of activated CF@CNP–30 and CF@CNP–60.

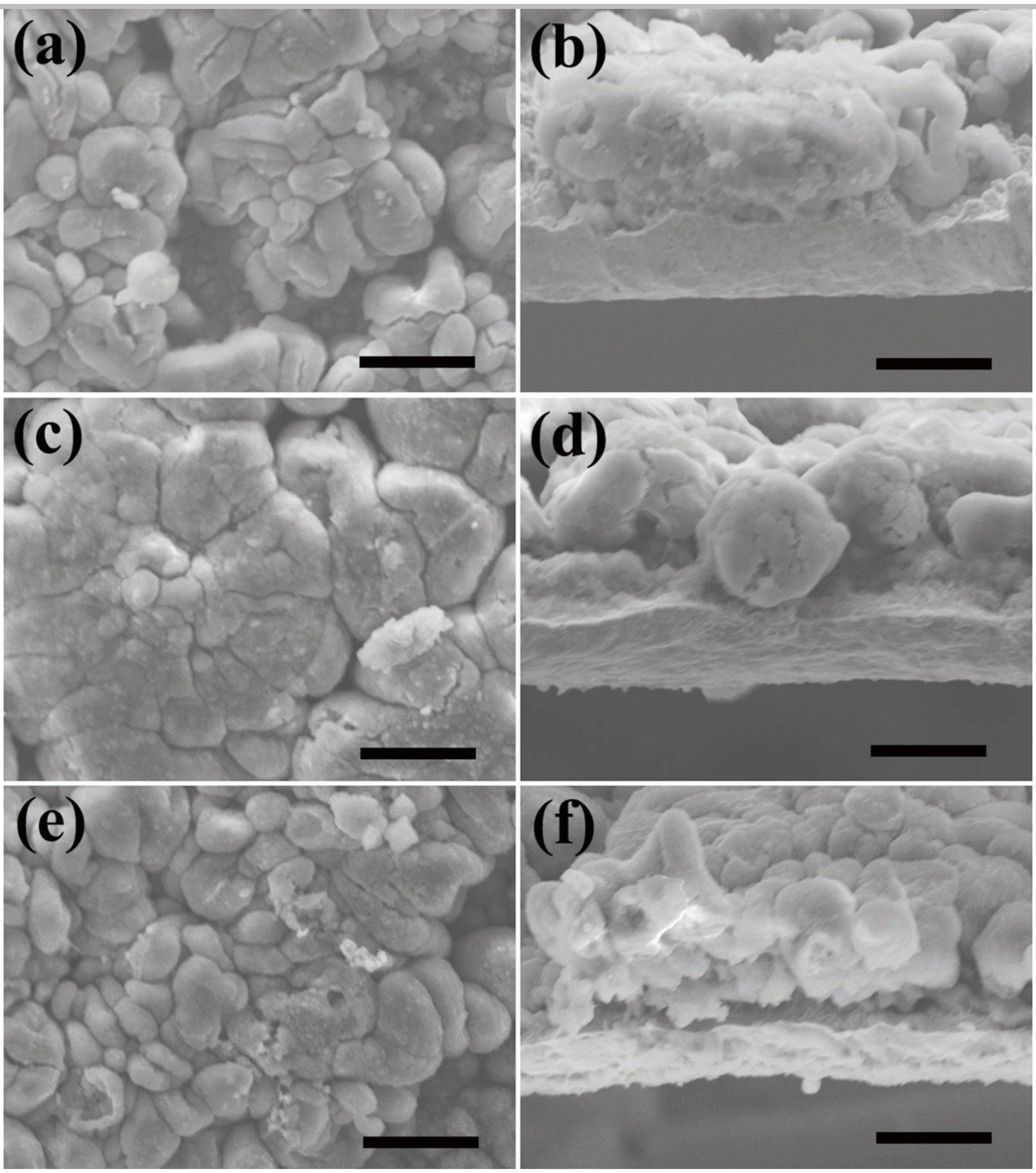

Fig. S6. SEM images of CF (a, b), CF@CNP–30 (c, d) and CF@CNP–60 (e, f) after the first lithium plating. Scale bars, 15 μm.

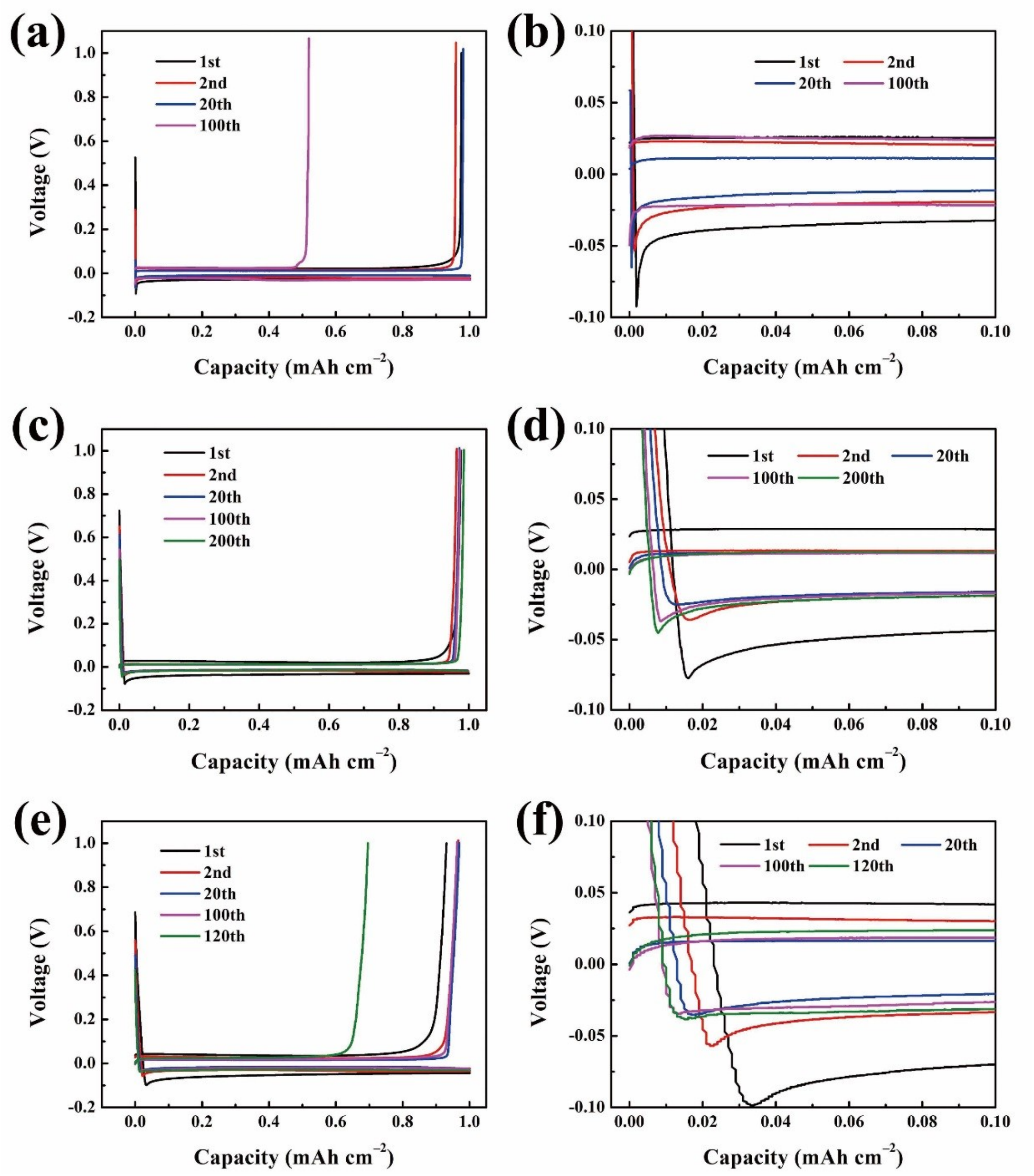

Fig. S7. (a) Typical voltage–capacity curves of (a) CF, (c) CF@CNP–30 and (e) CF@CNP–60 at 1 mA cm^{-2} after different cycles.

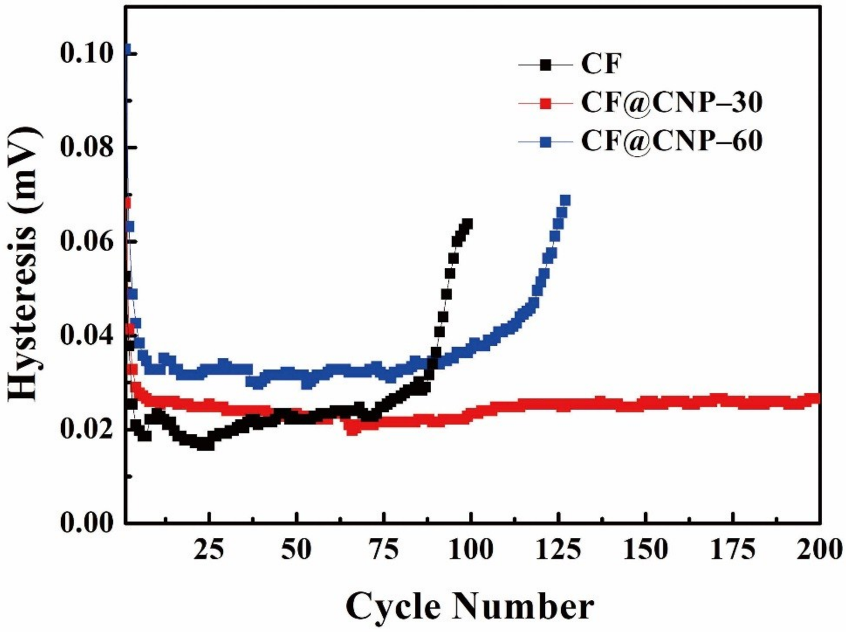

Fig. S8. Voltage hysteresis of CF, CF@CNP–30 and CF@CNP–60 at 1 mA cm^{-2}.

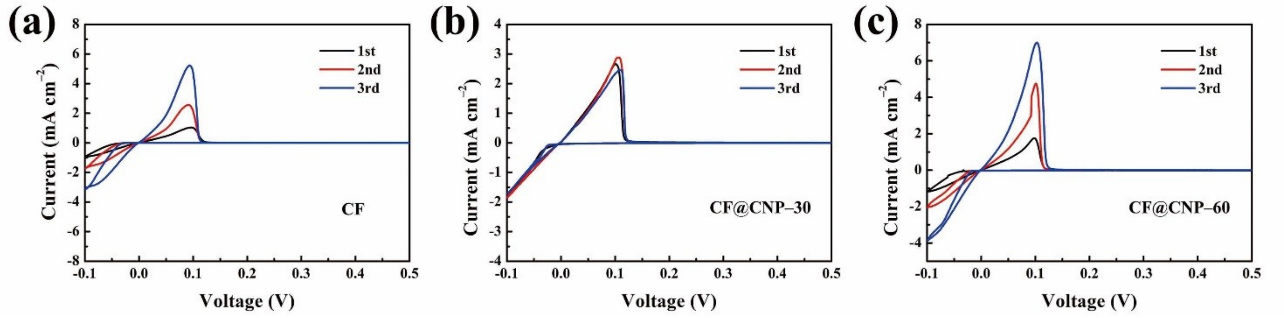

Fig. S9. CV curves of (a) CF, (b) CF@CNP–30 and (c) CF@CNP–60 with lithium counter electrode in the initial three cycles at 0.2 mV s^{-1} between −0.1 and 0.5 V.

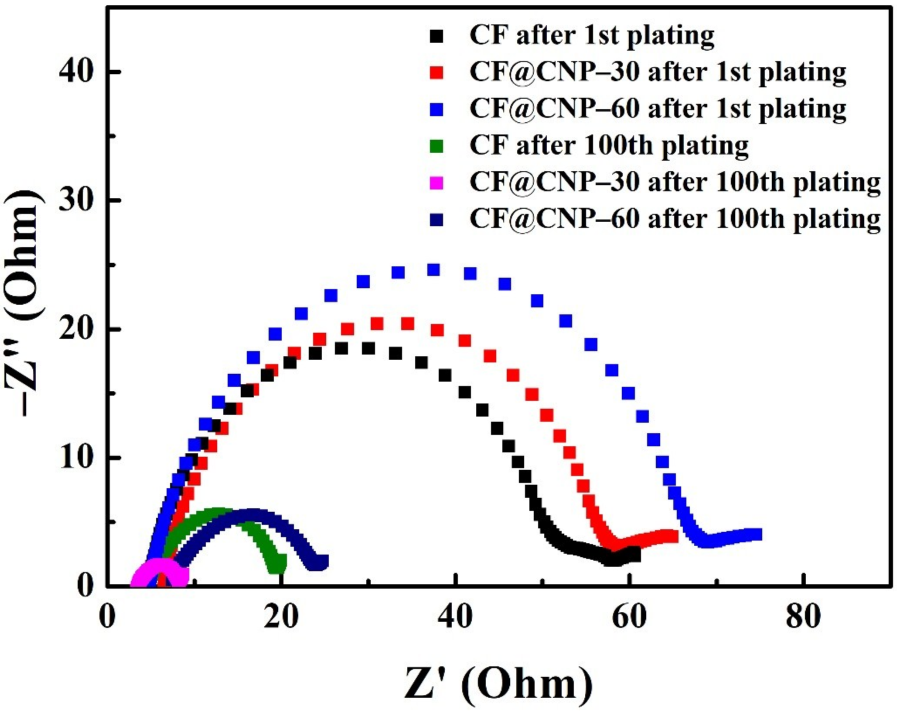

Fig. S10. EIS data of CF, CF@CNP-30 and CF@CNP-60 after 1st and 100th cycle.

Table S1. Comparison of the electrochemical performance of several materials.

Materials	Current density	Cycle number	Coulombic efficiency	Ref.
Graphitized carbon fibers	0.5 mA cm^{-2}	70	98%	1
graphene−carbon nanotube	2 mA cm^{-2}	225	99.6%	2
Cu-CuO-Ni hybrid structure	1 mA cm^{-2}	250	95%	3
CuO nanosheets on Cu collector	0.5 mA cm^{-2}	180	94%	4
$Cu_{99}Zn$ alloy	0.5 mA cm^{-2}	180	97%	5
Cu_2O nanoparticles decorated copper foil	1 mA cm^{-2}	200	99.5%	This work

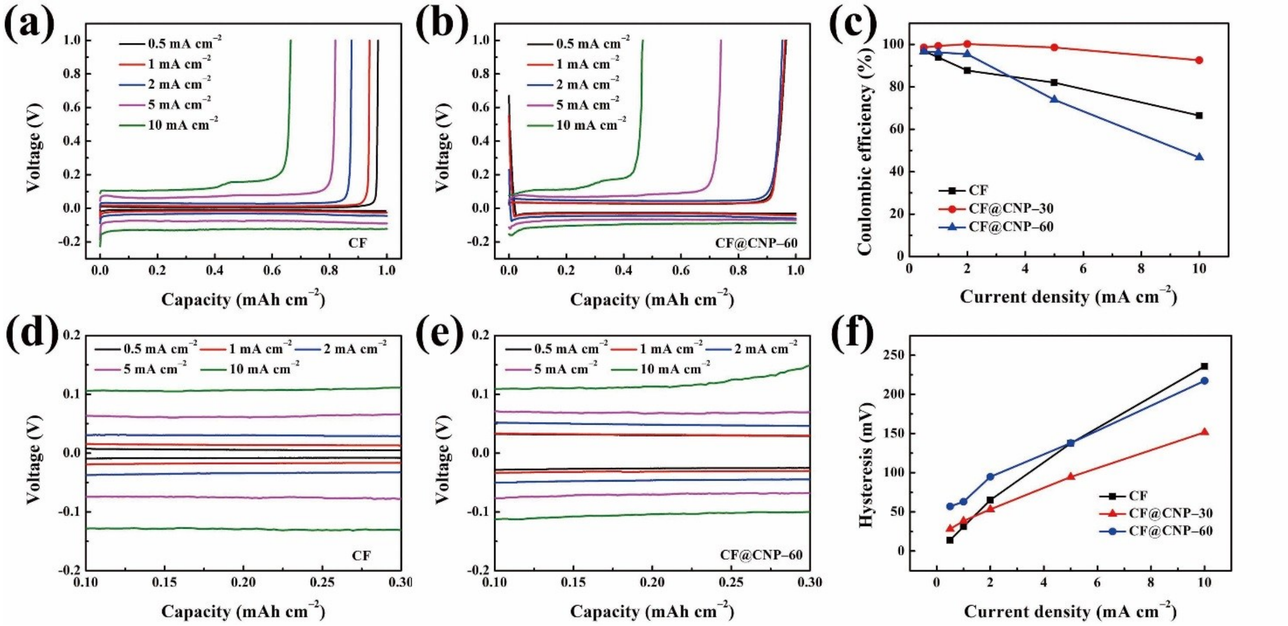

Fig. S11. Plating/stripping profiles of (a) CF and (b) CF@CNP–60 measured at different current densities. (c) Rate performance comparison of CF, CF@CNP–30 and CF@CNP–60. Magnified image of plating/stripping profiles of (d) CF and (e) CF@CNP–60 from 0.1 to 0.3 mAh cm^{-2}. (f) Voltage hysteresis comparison at different current densities.

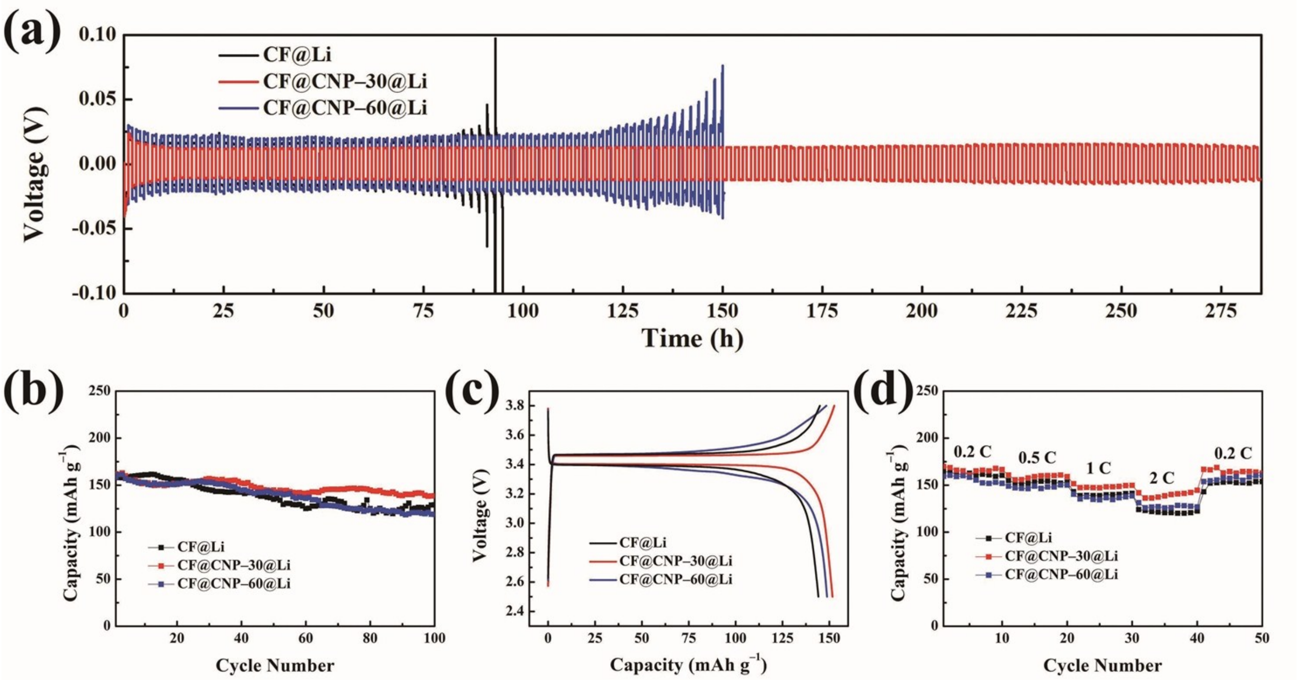

Fig. S12 (a) Galvanostatic plating/stripping profiles in symmetric cells. (b) Cycling performance of full cells at 0.5 C. (c) Voltage profiles of full cells in the 30th cycle at 0.5 C. (d) Rate performance of full cells.

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