Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Supporting Information

Direct Electrodeposition of Cobalt Oxide Nanosheets on Carbon Paper as Free-Standing Cathode for Li-O_2 Battery

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1. Chemicals and materials

Cobalt nitrate [$Co(NO_3)_2 \cdot 6H_2O$], tretraethylene glycol dimethyl ether (TEGDME), N-methyl-2-pyrrolidinone (NMP), lithium triflate ($LiCF_3SO_3$), and polyvinylidene Fluoride (PVDF) were purchased from Aladdin Reagent. Platinum electrode and calomel reference electrode (SCE) was purchased from Tianjin AidaHengsheng Tech. Co., China.

2. Synthesis

Synthesis of Co_3O_4 NSs/CP cathode

The electrodeposition was performed in a standard three-electrode glass cell consisting of the clean carbon paper working electrode, a platinum plate counter electrode, and a SCE reference electrode at room temperature. The amorphous Co_3O_4 was electrodeposited upon carbon paper in a 0.05 M $Co(NO_3)_2 \cdot 6H_2O$ aqueous electrolyte using an VMP3 Electrochemical Workstation (Biologic, Inc). The electrodeposition potential ranges from -1.2 to -0.8 V (vs. SCE). The scanning rate is 50 mV s^{-1}.

After electrodeposition for 50 cycles, the deposited carbon paper was carefully rinsed several times with deionized water and ethanol with the assistance of ultrasonication, and finally dried in air. The final product was obtained by calcination at 300 ℃ for 2 h.

Fabrication of Co_3O_4 NSs pasted on CP composite cathode

The Co_3O_4 NSs were scraped from Co_3O_4 NSs/CP and mixed with PVDF as a

binder with weight ratio of 4:1. Then, this composite was ball-milled to obtain a slurry mixture, which was then pasted onto CP and subsequently dried under vacuum at 80 ℃ for 12 h prior to use.

Assembly of Li-O_2 battery

The 2025-type coin cell was assembled in glove box under an argon atmosphere, using a clean lithium metal disk as the anode, a glass-fiber separator, and 1 M TEGDME- $LiCF_3SO_3$ based electrolyte.

3. Characterization

Samples for SEM were prepared by directing putting the electrode sample onto to a SEM brass stub. Transmission electron microscope (TEM) was performed using a FEI Tecnai G2 S-Twin instrument with a field emission gun operating at 200 kV. Samples dispersed in ethanol were deposited onto the Cu grid with carbon coated on Lacey support film and dried in air before TEM imaging. Powder X-ray diffraction (XRD) measurements were performed on a Bruker D8 Focus powder X-ray diffractometer using Cu K_α (λ = 0.15405 nm) radiation (40 kV, 40 mA). Nitrogen adsorption measurements were performed on a Micromeritics ASAP 2020 adsorption analyzer. FTIR was performed using A Thermo Nicolet 6700 FTIR spectrometer. Electrochemical impedance spectroscopy (EIS) measurements were performed on a BioLogic VMP3 electrochemical workstation (frequency range: 10^6 to 10^{-2} Hz). Li-O_2 cell measurements were cycled on a LAND CT 2001A multichannel battery testing system.

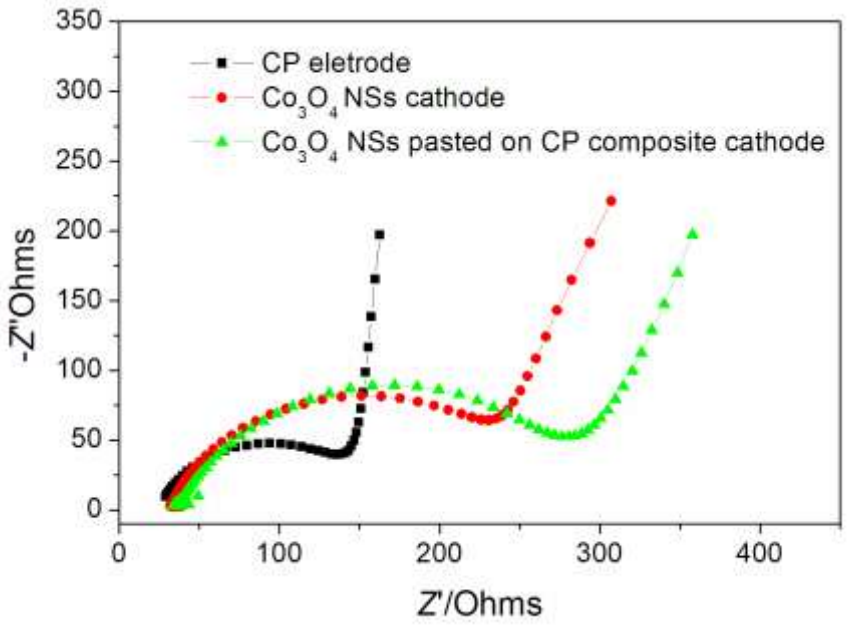

Fig. S1 Electrochemical impedance spectra measurements of three different cathodes.

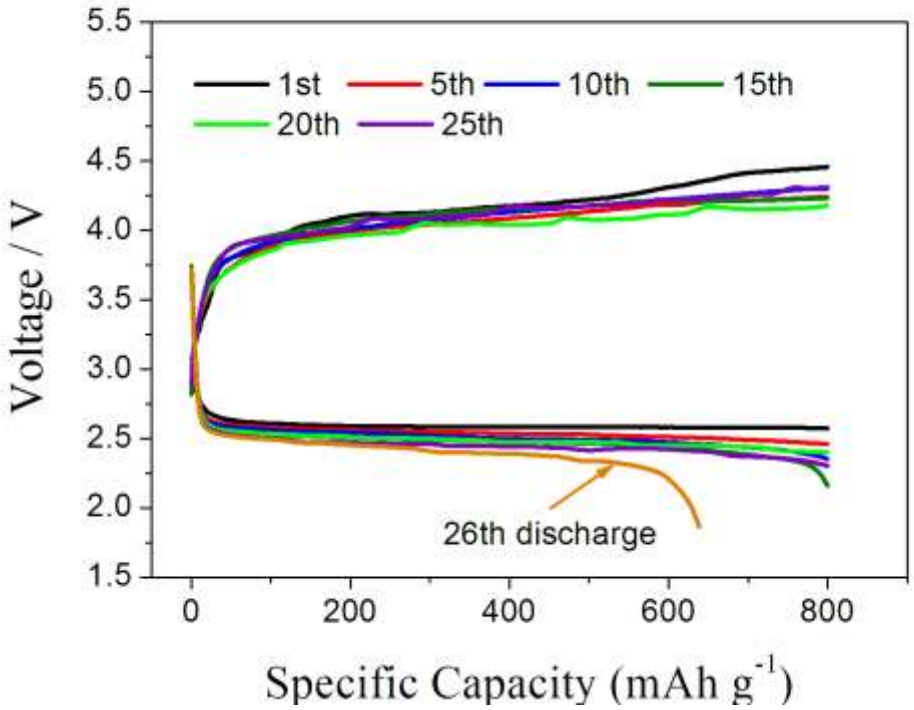

Fig. S2 Cycle performance of the Li-O_2 cell with Co_3O_4 NS/CP cathode with the capacity limited to 800 mA h g^{-1} at a current density of 100 mA g^{-1}.

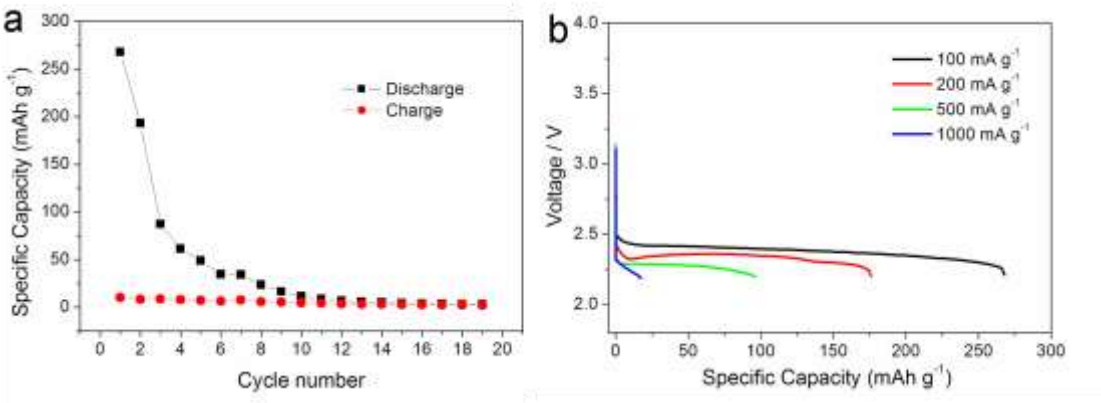

Fig. S3 (a) Cycle performance at current densities of 100 mA g^{-1} and (b) rate performance of Li-O_2 cell with pure CP cathode.

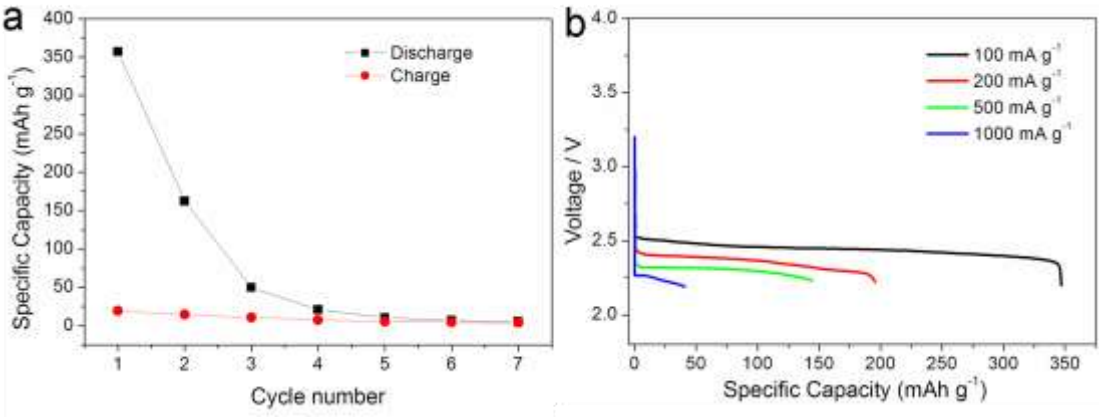

Fig. S4 (a) Cycle performance at current densities of 100 mA g^{-1} and (b) rate performance of Li-O_2 cell with Co_3O_4 NSs pasted on CP composite cathode.

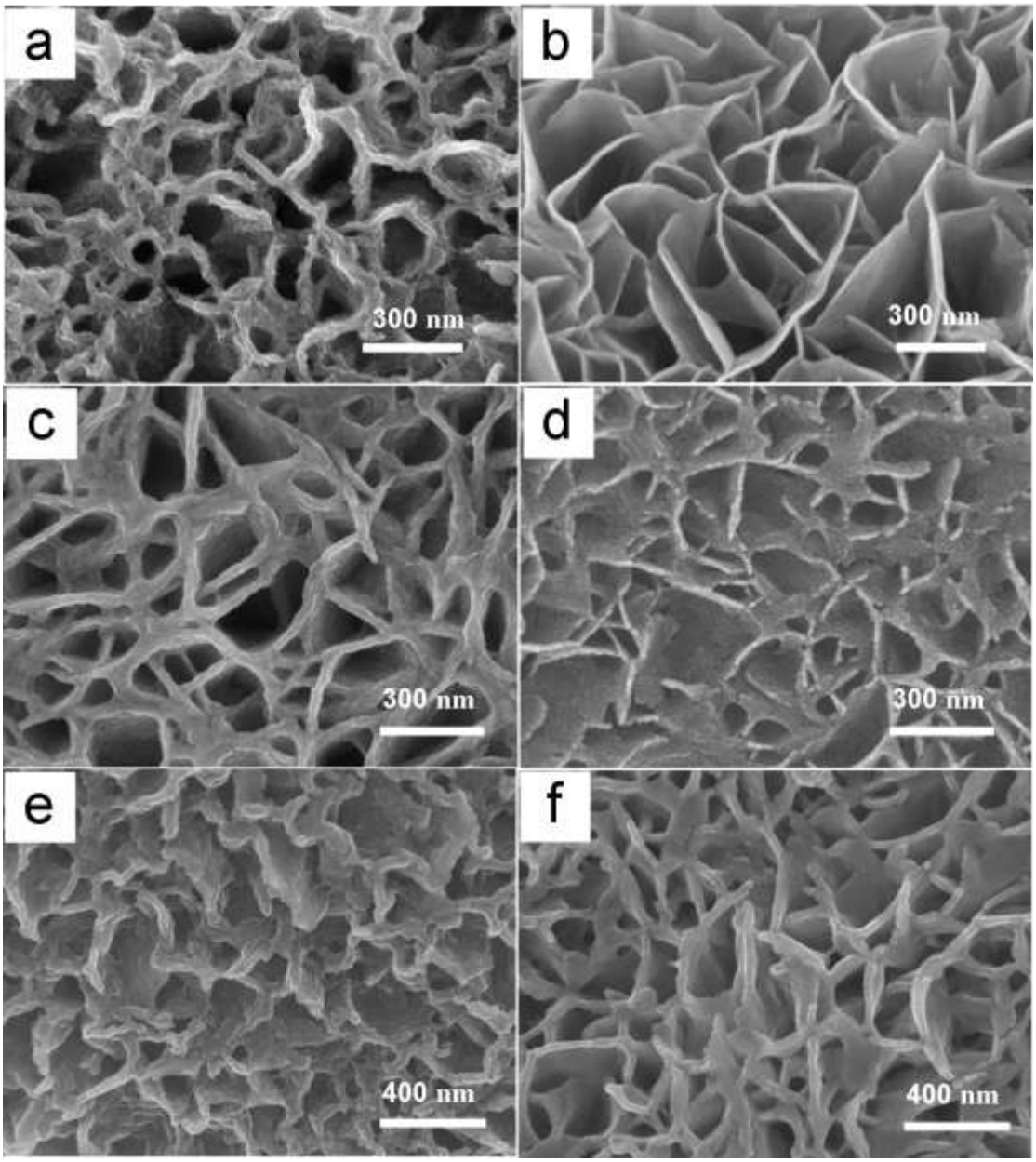

Fig. S5 SEM images of the Co_3O_4 NS/CP cathode (a) discharged and (b) charged after one cycle, (c) discharged and (d) charged after 10 cycles and (e) discharged and (f) charged after 26 cycles with the capacity limited to 800 mA h g^{-1}.

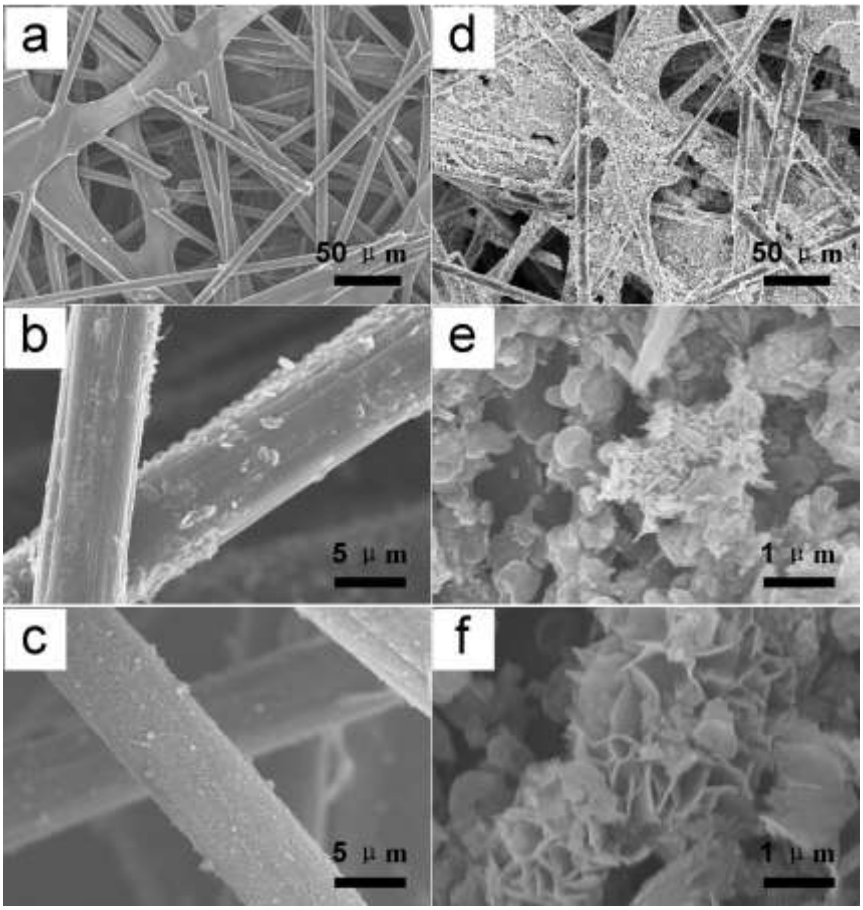

Fig. S6 SEM images of the CP and Co_3O_4 NSs pasted on CP composite cathodes. a, b and c are the pristine CP cathode, the CP cathode after the first discharge, and the CP cathode after the first recharged, respectively; d, e and f are the pristine Co_3O_4 NSs pasted on CP composite cathode, the Co_3O_4 NSs pasted on CP composite cathode after the first discharge, and the Co_3O_4 NSs pasted on CP composite cathode after the first recharged, respectively.

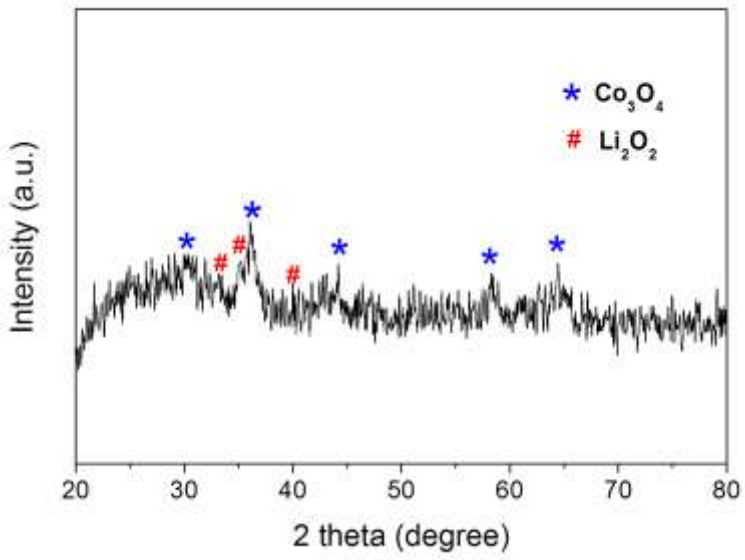

Fig. S7 XRD spectra of the Co_3O_4 NSs/CP cathode after the first discharged.