Supplementary Information

Carbon-Free Cobalt Oxide Cathodes with Tunable Nanoarchitectures for Rechargeable Lithium-Oxygen Batteries

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Materials synthesis

A Ni foam was treated with HCl for 30 min to remove residual oxide layers and was then washed with water and dried in air. A metallic cobalt layer was electrodeposited onto the Ni foam from a cobalt sulfate solution (0.26 M $CoSO_4 \cdot 7H_2O$) containing triethanolamine (0.53 M $(HOCH_2CH_2)_3N$). Electrodeposition was conducted at a current density of 10 mA cm^{-2} for 250 s using a Pt mesh as the counter electrode. The cobalt-deposited Ni foam was chemically treated with an oxalic acid solution (0.3 M $H_2C_2O_4$) containing water and ethanol. The water/ethanol volume ratio and the treatment time were varied to prepare cobalt oxalates with different morphologies. Finally, the specimen was thoroughly washed with ethanol and water, and heat-treated in air at 250°C for 2 h. The active area of the cathode was 0.785 cm^2 and the Co_3O_4 loading was maintained at *ca.* 0.6 mg cm^{-2}. For preparation of CNT buckypapers, the CNTs (50 mg) were dispersed in deionized water (50 mL) with Triton X-100 (500 mg) as a surfactant and then sonicated for 1 h. The well-dispersed CNT suspension was filtered through a polytetrafluoroethylene (PTFE) membrane with a 0.22 μm pore diameter under vacuum, and washed with water and methanol to remove any remaining surfactant. The resulting CNT buckypaper was peeled off of the PTFE membrane and dried under vacuum at 60°C for 12 h.

Materials characterization

To identify the crystal structures of the synthesized materials, XRD patterns were recorded with an automated Rigaku diffractometer (2500 D/MAX, Rigaku) using Cu K_α (λ = 1.5405 Å) radiation. The measurements were conducted over the scanning angle range of 10 – 80° at a scan rate of 5° min^{-1}. The morphology and microstructure were examined by SEM (Hitach X-4900) and TEM (Hitachi H9000). The BET surface area was determined from N_2

sorption isotherms by using a BEL-SORP mini system. XPS was conducted using a Thermo MultiLab 2000 spectrometer with a monochromatic Al K_α X-ray source. To avoid any contamination, the discharged electrode was transferred from the Ar-filled glove box to the XPS chamber using a specially designed air-proof chamber.

Electrochemical Experiments

Li-O_2 cells were constructed based on a Swagelok design and were composed of a Li metal anode, an electrolyte (1 M LiTFSI in TEGDME) impregnated into a glass fiber separator and a cathode. Discharge-charge profiles were measured at a current density of 20 or 100 mA g^{-1} (based on the mass of Co_3O_4 or carbon) using a Maccor Series 4000. For cycling experiments, batteries were discharged at 100 mA g^{-1} and were then charged using a protocol of constant current (CC)-constant potential (CP), *viz.*, CC charge with 100 mA g^{-1} to either 4.2 or 4.6 V *vs.* Li/Li^+ followed by CP charge with a 20 mA g^{-1} cut-off current.

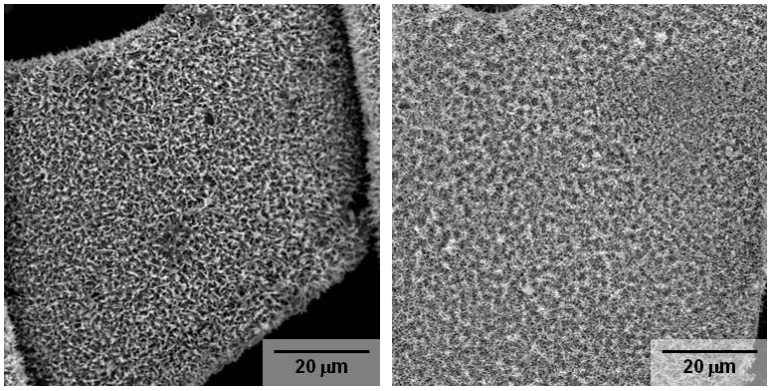

Fig. S1 SEM micrographs of the cobalt oxide with NN-like morphology.

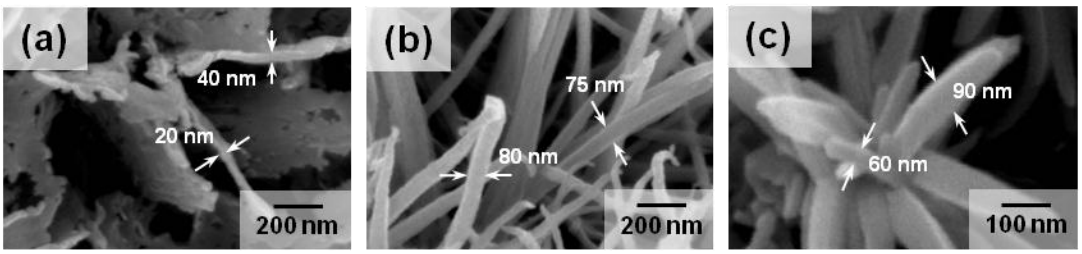

Fig. S2 SEM micrographs of the cobalt oxides with (a) NS-, (b) NN-, and (c) NF-like morphologies.

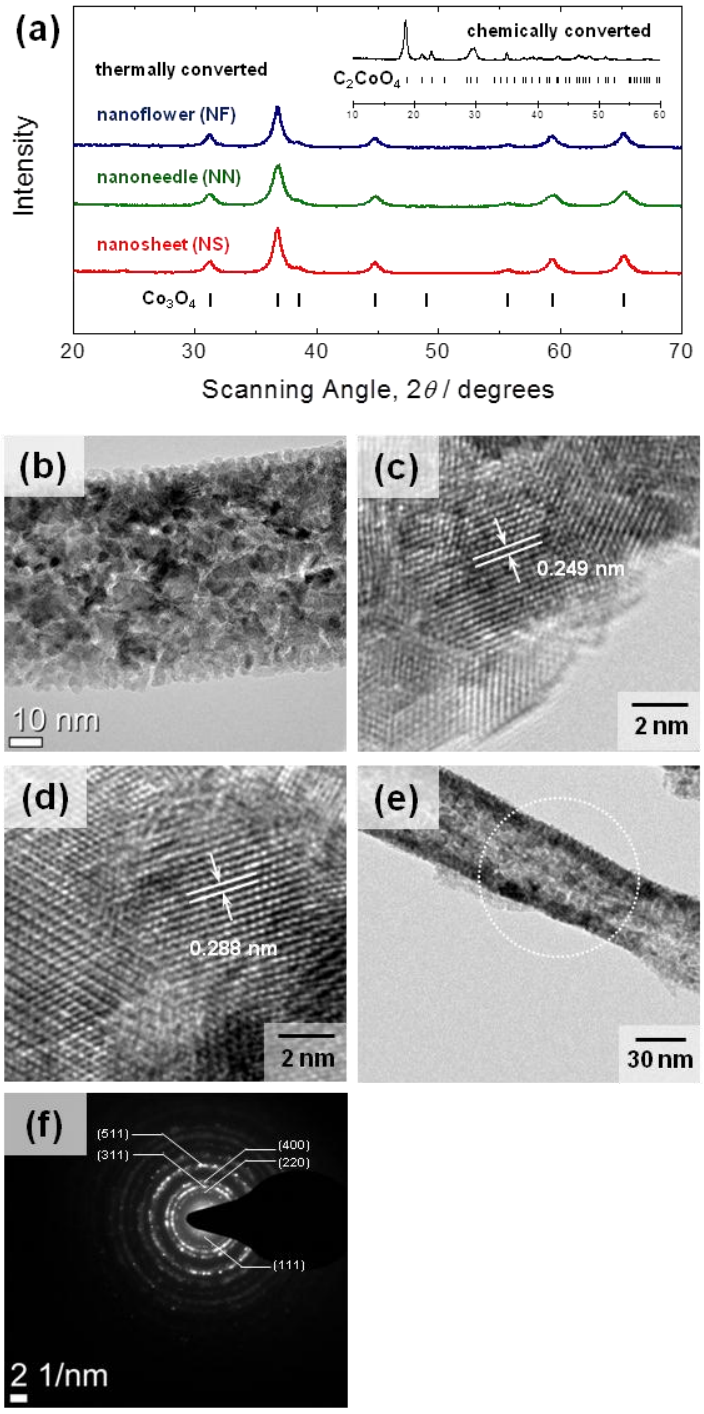

Fig. S3 (a) XRD patterns of the cobalt oxalates and oxides (taken out of the substrate), (b)–(e) TEM micrographs for the nanoneedle-like cobalt oxide, and (f) SAED pattern measured over the area designated by the circle in (e).

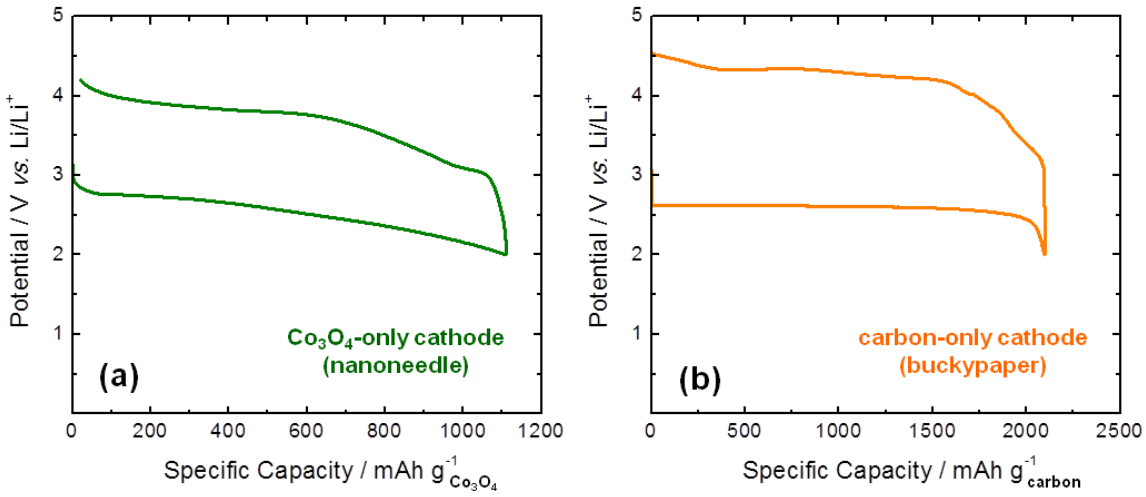

Fig. S4 Discharge-charge profiles of (a) the Co_3O_4-only (nanoneedles) and (b) carbon-only cathodes (buckypaper) measured at 100 mA g^{-1} (based on the Co_3O_4 or carbon weight). The electrolyte was 1 M LiTFSI in TEGDME. Note that Co_3O_4 has a higher mass than carbon, resulting in a relatively low specific capacity compared with the capacity reported for carbon.

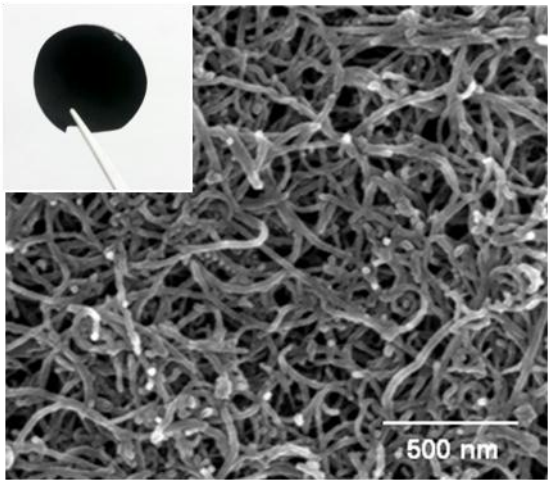

Fig. S5. SEM micrograph of the carbon-only cathode prepared in the form of a CNT buckypaper (see the inset).

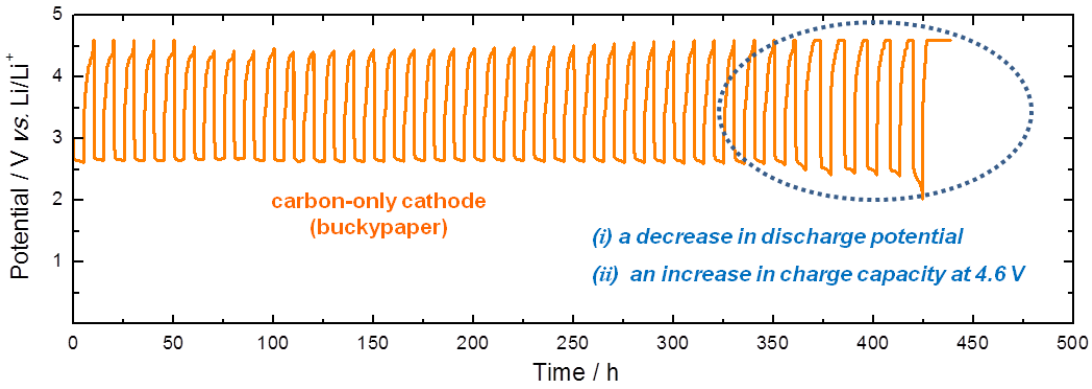

Fig. S6 Cycling performance of the carbon-only cathode measured at 100 mA g^{-1} (based on the carbon weight).