Supporting Information

Self-supporting Co$_3$O$_4$ with lemongrass-like morphology as a high-performance anode material for lithium ion batteries

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Experimental details

Sample preparation: For in-situ growth of Co$_3$O$_4$ on Ni foam, 1 mmol of Co(NO$_3$)$_2$•6H$_2$O and 10 mmol of CO(NH$_2$)$_2$ were dissolved into 50 mL deionized water under vigorous stirring. After stirring for 20 min, the homogeneous solution was transferred into a Teflon-lined stainless steel autoclave with a volume of 80 mL, and then a piece of cleaned Ni foam (with an area of 2×3 cm$^2$) was immersed into it. The autoclave was tightly sealed and heated at 90 °C for 6 h in an oven, then cooled down to room temperature naturally. The Ni foam with purple precursors grown was fetched out and rinsed with deionized water several times. Finally, the as-synthesized precursors were annealed at 350 °C for 1 h in air.

Structural characterization: The crystalline structures and morphologies of the samples were characterized by X-ray diffraction (XRD, X' Pert PRO PHILIPS, Cu K$\alpha$ radiation, $\lambda$=1.54056 Å), micro-Raman spectrometer (Raman, Jobin-Yvon LabRAM HR800) with a radiation of 532 nm, field emission scan electron microscopy.

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(FE-SEM, Hitachi S-4800), and high-resolution transmission electron microscopy (HRTEM, FEI, Tecnai G² F30).

**Electrochemical characterizations:** Electrochemical characterizations were carried out with CR2032 coin type half cells by using the grown Co₃O₄ on Ni foam as the working electrode and lithium foil as the counter and reference electrodes. The cell preparation process has been described in our previous paper.[1] Celgard 2320 was used as the separator membrane. The electrolyte was 1 M lithium hexafluorophosphate (LiPF₆) dissolved in ethylene carbonate: dimethyl carbonate: ethyl methyl carbonate in a 1:1:1 volume ratio. The cyclic voltammetry and galvanostatic discharge-charge cycling were carried out at room temperature by using an electrochemical workstation (CHI 660C) and a multichannel battery tester (Neware BTS-610), respectively.

**Supporting figures**

*Figure S1.* Low-magnification and high-magnification images of the precursor on Ni foam. The lemongrass-like morphologies of the samples before and after annealing in air are similar, which were grown directly on the substrate of Ni foam in a large area.
**Figure S2.** XRD pattern of the precursor on Ni foam. Besides the diffraction peaks marked “#” from the Ni foam substrate, the other obvious diffraction peaks can be indexed to the orthorhombic Co(CO$_3$)$_{0.5}$(OH)-0.11H$_2$O (JCPDS card No. 48-0083), showing that the cobalt carbonate hydroxide hydrate precursor has been grown on Ni foam.

**Figure S3.** XRD patterns of the sample after annealing in air. Besides the diffraction peaks marked “#” from the Ni foam substrate, the other diffraction peaks can be indexed to (111), (220), (311), (222), (422), (511) and (440) lattice planes of spinel Co$_3$O$_4$, respectively (JCPDS Card No. 42-1467), indicating that the cobalt carbonate
hydroxide hydrate precursor was turned into crystalline Co$_3$O$_4$ completely.

**Figure S4.** Raman spectrum of the sample after annealing in air. The peaks centered at 187, 466, 512, 609, and 674 cm$^{-1}$, can be attributed to the F$_{2g}$, E$_g$, F$_{2g}$, F$_{2g}$, and A$_{1g}$ vibration modes of spinel Co$_3$O$_4$ phase,$^2$ respectively, which is consistent with the results of SAED, HRTEM and XRD examinations.

**Figure S5** SEM images of the self-supporting Co$_3$O$_4$ electrode after 100 discharge/charge cycles at a rate of 0.5 C. It can be seen that no obvious exfoliation can be found and the lemongrass-like morphology was remained perfectly.
Figure S6. A schematic diagram for Li$^+$ insertion/extraction of self-supporting Co$_3$O$_4$ with lemongrass-like morphology on Ni foam electrode.

References
