Supporting Information

Self-supporting Co_3O_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_3O_4 on Ni foam, 1 mmol of $Co(NO_3)_2$•$6H_2O$ 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 Kα radiation, λ=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 G^2 F30).

Electrochemical characterizations: Electrochemical characterizations were carried out with CR2032 coin type half cells by using the grown Co_3O_4 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 ($LiPF_6$) 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

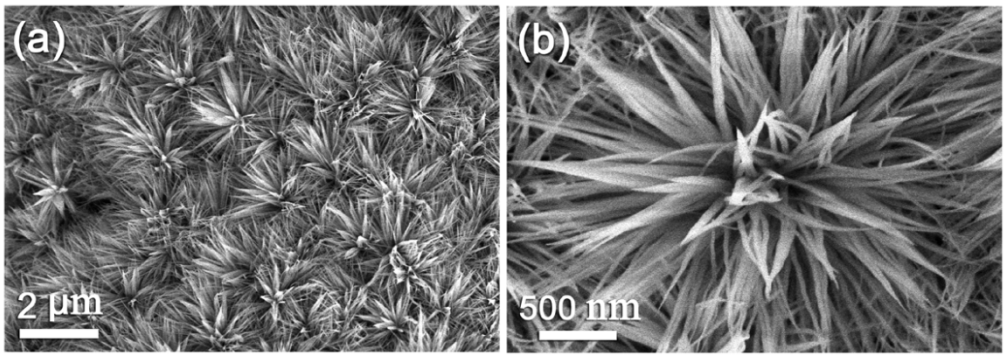

Figure S1. Low-magnification and high-magnification images of the precursor on Ni foam. The lemongrass-like morphologies of the samples before and after annealing in air are similar, which were grown directly on the substrate of Ni foam in a large area.

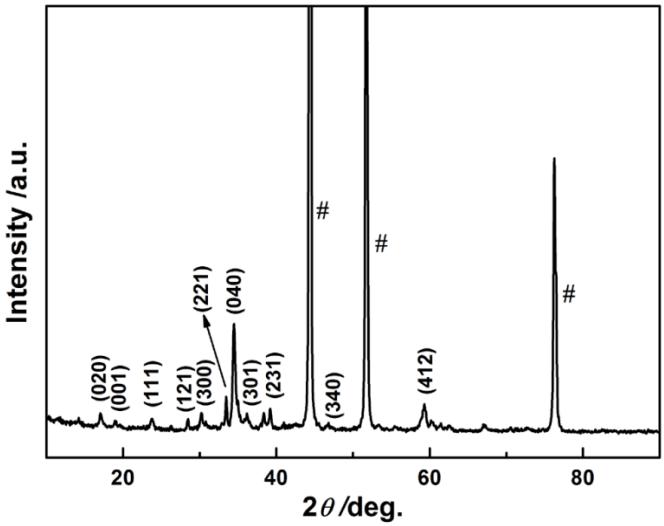

Figure S2. XRD pattern of the precursor on Ni foam. Besides the diffraction peaks marked "#" from the Ni foam substrate, the other obvious diffraction peaks can be indexed to the orthorhombic $Co(CO_3)_{0.5}(OH)\cdot 0.11H_2O$ (JCPDS card No. 48-0083), showing that the cobalt carbonate hydroxide hydrate precursor has been grown on Ni foam.

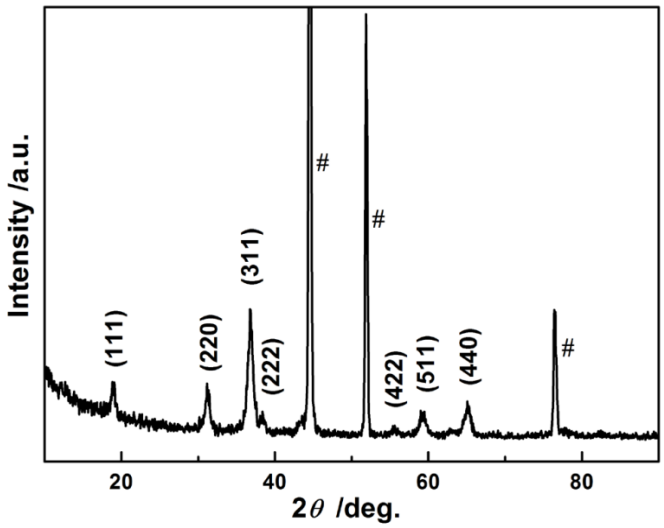

Figure S3. XRD patterns of the sample after annealing in air. Besides the diffraction peaks marked "#" from the Ni foam substrate, the other diffraction peaks can be indexed to (111), (220), (311), (222), (422), (511) and (440) lattice planes of spinel Co_3O_4, respectively (JCPDS Card No. 42-1467), indicating that the cobalt carbonate

hydroxide hydrate precursor was turned into crystalline Co_3O_4 completely.

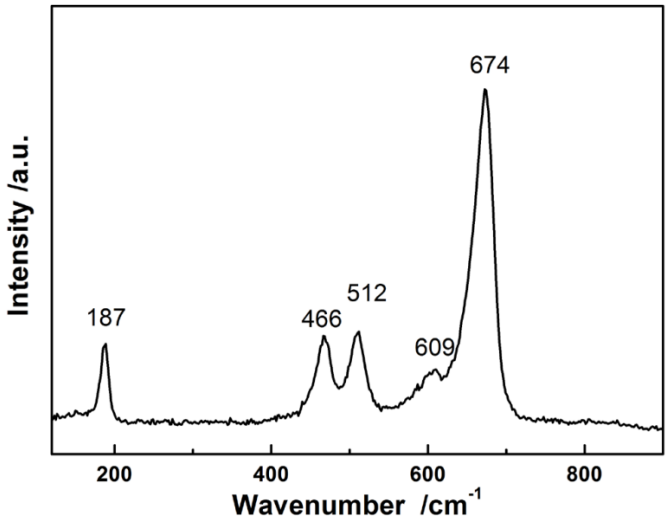

Figure S4. Raman spectrum of the sample after annealing in air. The peaks centered at 187, 466, 512, 609, and 674 cm^{-1}, can be attributed to the F_{2g}, E_g, F_{2g}, F_{2g}, and A_{1g} vibration modes of spinel Co_3O_4 phase,[2] respectively, which is consistent with the results of SAED, HRTEM and XRD examinations.

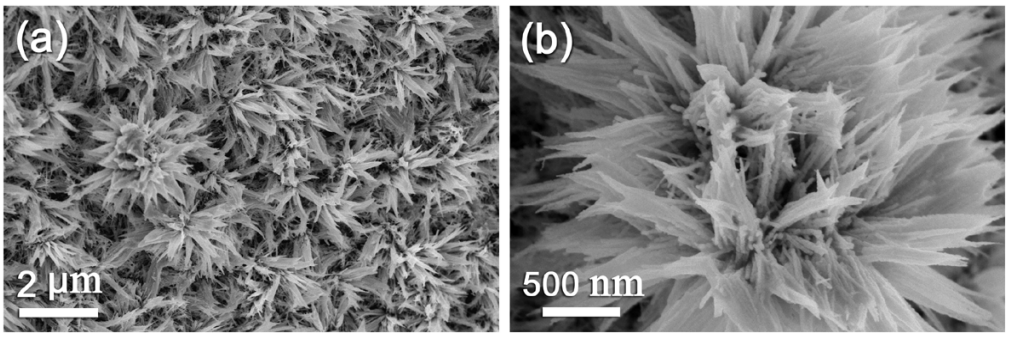

Figure S5 SEM images of the self-supporting Co_3O_4 electrode after 100 discharge/charge cycles at a rate of 0.5 C. It can be seen that no obvious exfoliation can be found and the lemongrass-like morphology was remained perfectly.

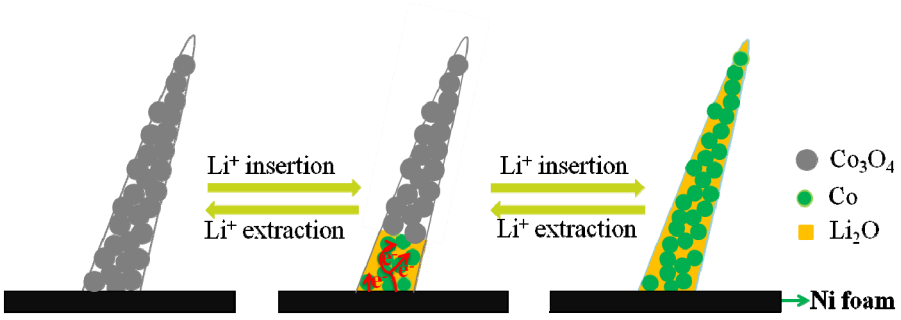

Figure S6. A schematic diagram for Li^+ insertion/extraction of self-supporting Co_3O_4 with lemongrass-like morphology on Ni foam electrode.

References

[1] X.W. Li, D. Li, L. Qiao, X.H. Wang, X.L. Sun, P. Wang, D.Y. He, J. Mater. Chem. 22 (2012) 9189.

[2] V.G. Hadjiev, M.N. Iliev, I.V. Vergilov, J. Phys. C: Solid State Phys. 21 (1988) L199.