Supplementary Information

Mushroom-like Au/NiCo₂O₄ nanohybrid as high-performance binder-free

catalytic cathode for lithium-oxygen batteries

Fangfang Tu,^a Jian Xie,^{*ab} Shichao Zhang,^c Gaoshao Cao,^b Tiejun Zhu^a and Xinbing Zhao^{ab}

- ^aState Key Laboratory of Silicon Materials, School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China
- ^bKey Laboratory of Advanced Materials and Applications for Batteries of Zhejiang Province, Hangzhou 310027, China
- ^cSchool of Materials Science and Engineering, Beijing University of Aeronautics and Astronautics, Beijing 100191, China

^{*}E-mail: xiejian1977@zju.edu.cn; Fax: +86-571-87951451; Tel: +86-571-87952181



Fig. S1 (a) SEM image of 3D-G, (b) enlarged view of (a), and (c) Raman spectrum of 3D-G.



Fig. S2 (a) Nitrogen adsorption and desorption isotherms and (b) pore size distribution of $Au/NiCo_2O_4/3D$ -G, and (c) nitrogen adsorption and desorption isotherms and (d) pore size distribution of $NiCo_2O_4/3D$ -G.



Fig. S3 SEM images of NiCo₂O₄/3D-G on Ni foam after impregnation in aqueous solution of (a)

HCl, (b) H₂PtCl₆, (c) Na₂PdCl₄, and (d) Na₂PdCl₄ with HCl.



Fig. S4 (a) SEM image of Au/NiCo₂O₄/3D-G and (b) the corresponding EDS mapping.



Fig. S5 Nyquist plots of Li– O_2 batteries with different catalytic cathodes. The Nyquist plots are fitted using the equivalent circuit in the inset, where R_e denotes the electrolyte and ohm resistance, R_f and Q_1 are the resistance and capacitance of surface film, R_{ct} and Q_2 are the charge transfer resistance and double-layer capacitance, and Z_w represents the Warburg impedance corresponding to the bulk diffusion of Li ions.

Sample	$R_{\rm e}\left(\Omega\right)$	$R_{\rm f}(\Omega)$ -	Q_1		P(0)	Q_2	
			Y	п	$\Lambda_{\rm ct}$ (22)	Y	n
Au/3D-G	150.7	118.4	1.5×10^{-5}	0.77	98.9	1.1×10 ⁻⁴	0.96
Au/NiCo ₂ O ₄ /3D-G	283.4	259.4	7.1×10-6	0.90	271.3	7.4×10 ⁻⁴	0.38
NiCo ₂ O ₄ /3D-G	589.4	523.4	1.0×10^{-5}	0.93	688.4	5.5×10 ⁻⁴	0.30
Au/NiCo ₂ O ₄	286.6	818.7	1.4×10^{-5}	0.91	316.6	1.3×10 ⁻³	0.33

Table S1 Fitting results of the Nyquist plots using the equivalent circuit.



Fig. S6 (a) The first discharge-charge curve and (b) cycling performance of $\text{Li}-O_2$ battery with 3D-G electrode, and (c) the first discharge-charge curve and (d) cycling performance of $\text{Li}-O_2$ battery with Au/3D-G electrode. The current density is 42.5 mA g⁻¹ and the specific capacity is limited at 510 mAh g⁻¹.



Fig. S7 (a) TEM image and the corresponding SAED patterns of Au/NiCo₂O₄/3D-G electrodes after (b) discharge and (c) charge to 510 mAh g^{-1} at 42.5 mA g^{-1} .



Fig. S8 Nyquist plots of Li– O_2 battery with Au/NiCo₂O₄/3D-G electrode at initial state, discharged to 2.2 V, and recharged to 4.3 V. The meanings of the symbols in the equivalent circuit are same with those in Fig. S5.

Table S2 Fitting results of the Nyquist plots using the equivalent circuit.

Sample	$R_{\rm e}\left(\Omega ight)$	$R_{ m f}(\Omega)$	Q_1		P(0)	Q_2	
			Y	n	$\Lambda_{\rm ct}$ (32)	Y	n
Initial	283.4	259.4	7.1×10 ⁻⁶	0.90	271.3	7.4×10 ⁻⁴	0.38
After discharge	296.0	631.2	9.8×10-6	0.92	503.2	1.0×10 ⁻³	0.28
After recharge	270.0	209.7	4.0×10 ⁻⁵	0.91	206.9	3.0×10 ⁻⁴	0.33



Fig. S9 SEM images of NiCo₂O₄/3D-G electrode after (a) discharge and (b) recharge to 510 mAh

 g^{-1} at 42.5 mA g^{-1} on the 10 th cycle.



Fig. S10 SEM images and Li1s XPS of Au/NiCo₂O₄/3D-G electrodes at different states: (a) SEM

image after the 45th discharge, (b) SEM image after the 45th charge and (c) Li1s XPS after the 45th cycle. The batteries are charged and discharged to 510 mAh g^{-1} at 42.5 mA g^{-1} .