

Supporting Information

Hierarchical Mesoporous/Macroporous Perovskite $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-x}$ Nanotubes: a Bi-functional Catalyst with Enhanced Activity and Cycle Stability for Rechargeable Lithium Oxygen Batteries

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Details of kinetic analysis:

The oxygen reduction reaction (ORR) polarization curves were measured in O₂ saturated 0.1 M KOH solution at 5 mV s⁻¹ under different rotation rate from 400 rpm to 2025 rpm. Transfer electron numbers per oxygen molecule in the ORR was determined by the K-L equations as follows:^{S1}

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B\omega^{1/2}} \quad (1)$$

where j is the measured current density, j_k is the kinetic current density and ω is the angular velocity of the disk ($\omega=2\pi N$, N is the linear rotation speed).

$$B = 0.62nFC_{O_2}(D_{O_2})^{2/3}\nu^{-1/6} \quad (2)$$

where n represents the overall number of electrons gained per oxygen, F is the Faraday constant ($F=96485 \text{ C mol}^{-1}$), C_{O_2} is the bulk concentration of O₂ ($1.21 \times 10^{-3} \text{ mol L}^{-1}$), D_{O_2} is the diffusion coefficient of O₂ in 0.1 M KOH electrolyte ($1.86 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), ν is the kinetic viscosity of the electrolyte ($1.009 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$).

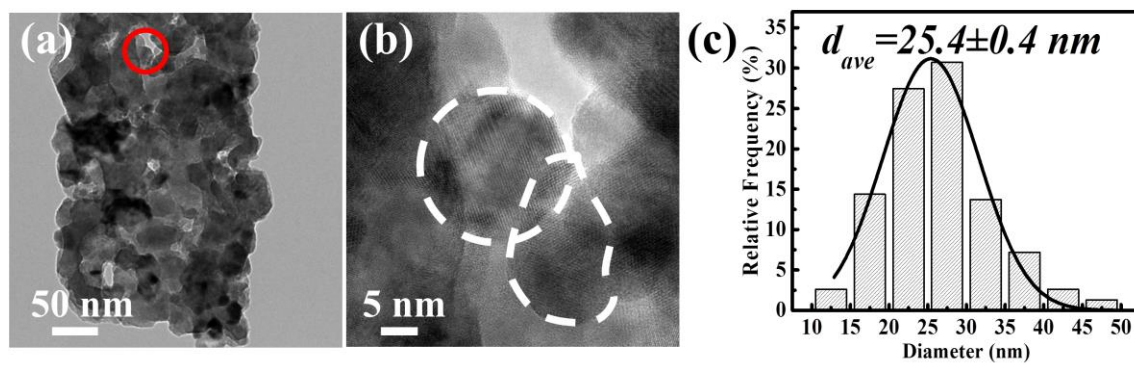


Figure S1. a) TEM image, b) HRTEM image c) histogram of diameter distributions of the synthesized HPN-LSC

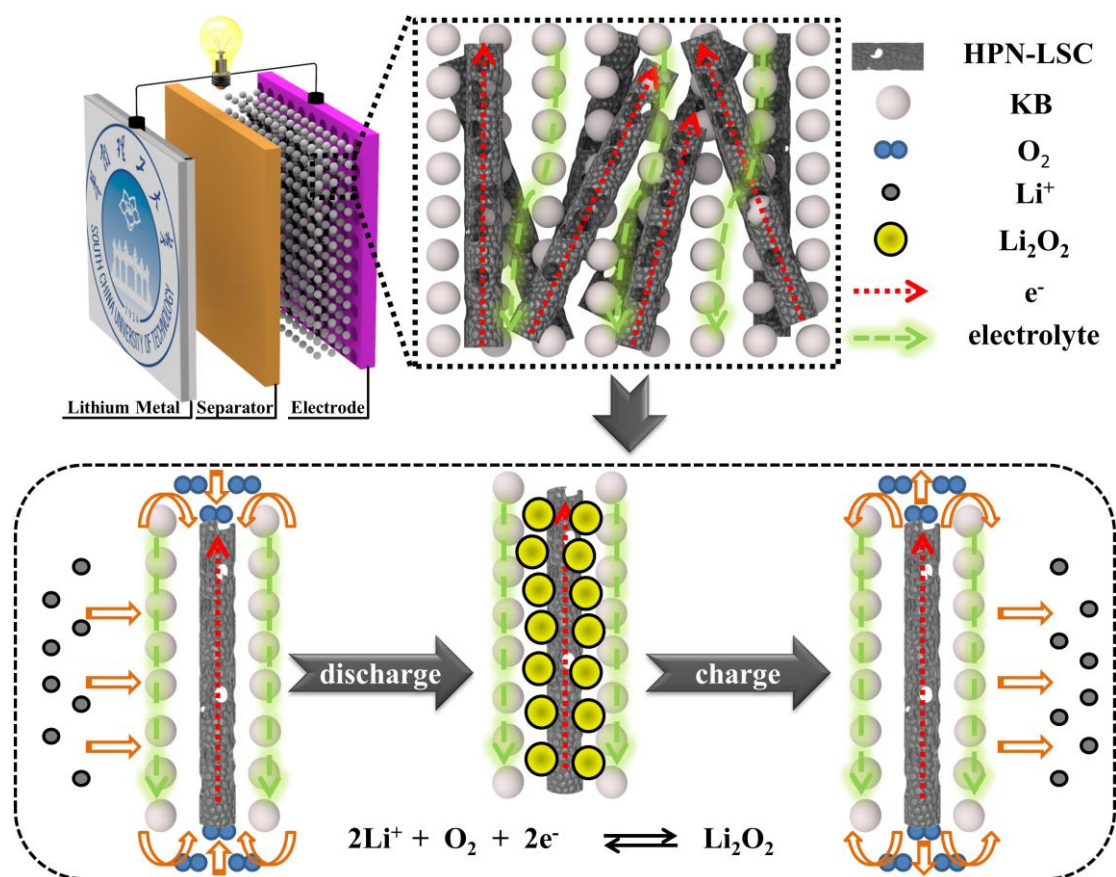


Figure S2. Structure of a rechargeable Li-O₂ battery with HPN-LSC catalysts and the working mechanism of the oxygen electrode containing HPN-LSC.

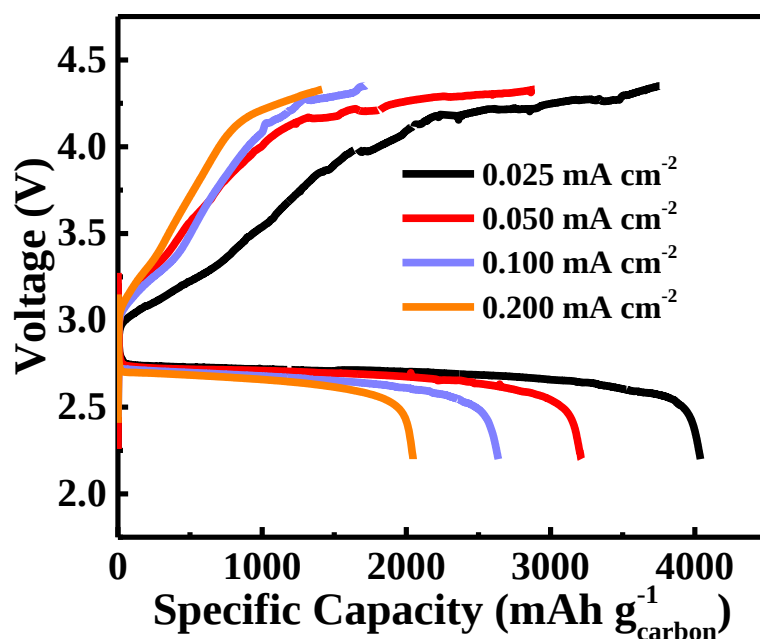


Figure S3. Discharge/charge profiles of Li-O₂ batteries with pure KB electrode at various current densities.

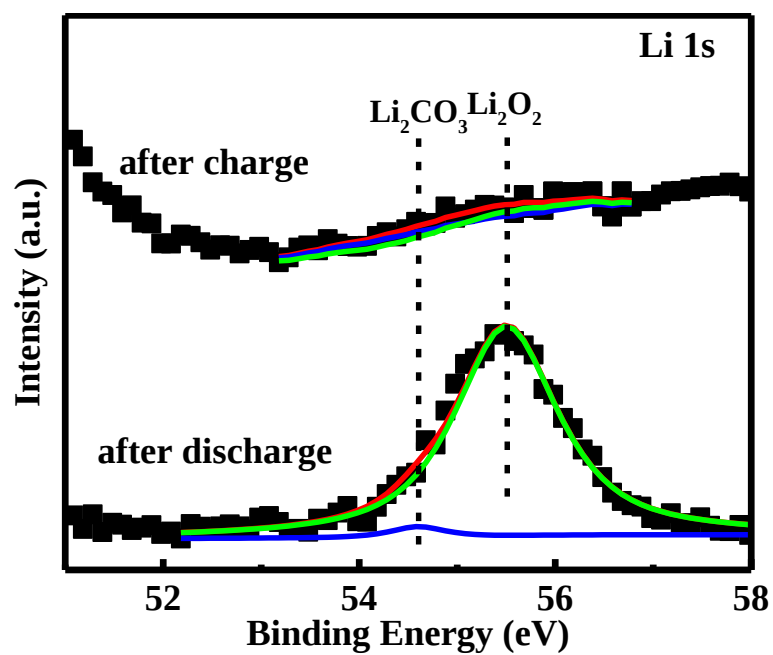


Figure S4. Li 1s XPS spectra of the HPN-LSC/KB electrode after discharge and after charge.

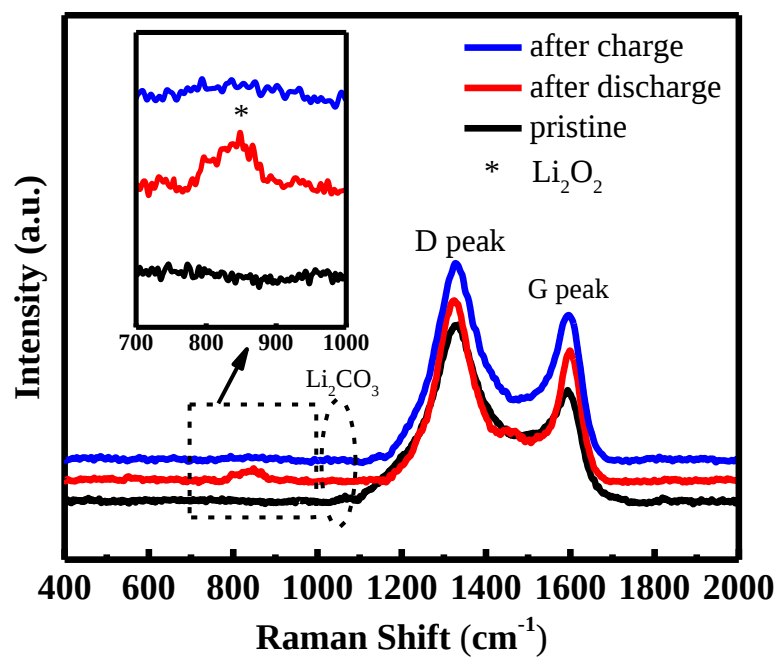


Figure S5. Raman spectra of HPN-LSC electrode before discharge, after discharge and after charge.

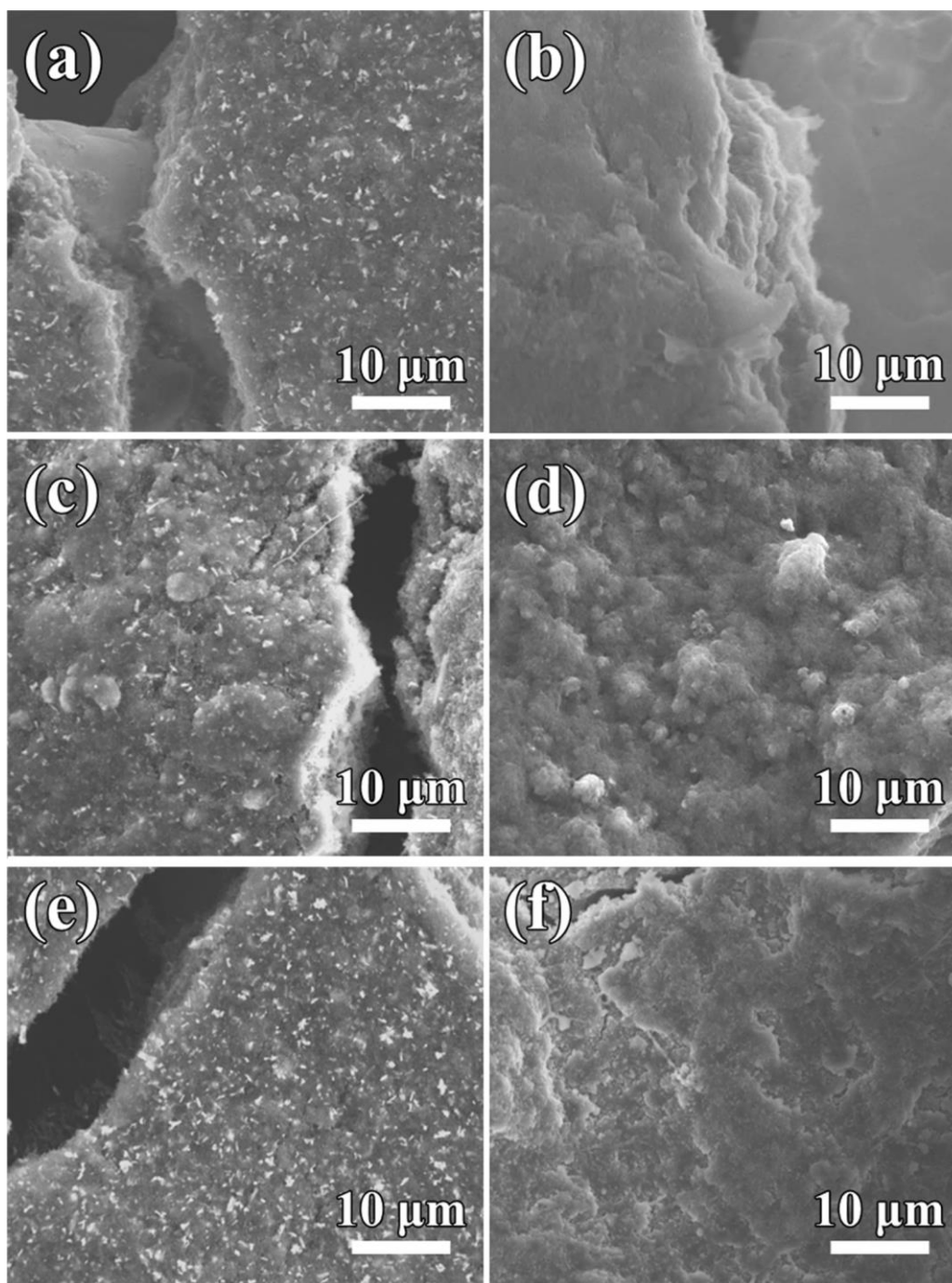


Figure S6. SEM images of HPN-LSC/KB electrode (a, c, e) and pure KB electrode (b, d, f) before 1st discharge (a, b) after 1st discharge (c, d) and after 1st charge (e, f).

Table S1. Comparison of electrochemical performance between the current work and micron-scale or nano-scale structured catalysts for Li-O₂ batteries.

Material	Current Density	Maximum Capacity	Upper-limit Capacity	Cyclic performance	Reference
mesoporous/macroporous La_{0.5}Sr_{0.5}CoO_{3-x} nanotubes	0.025 mA cm⁻² (50 mA g⁻¹)	5799 mAh g⁻¹ carbon 3866 mAh g⁻¹ carbon+catalyst	500 mAh g⁻¹	50 cycles at 0.100 mA cm⁻² (200 mA g⁻¹)	This work
mesoporous La _{0.5} Sr _{0.5} CoO _{2.91} nanowires	42 mA g ⁻¹	11059 mAh g ⁻¹	-	1cycle at 42 mA g ⁻¹	S2
La _{1.7} Ca _{0.3} Ni _{0.75} Cu _{0.25} O ₄ Particles	40 mA g ⁻¹	1600 mAh g ⁻¹ carbon	700 mAh g ⁻¹	15 cycles at 80 mA g ⁻¹	S3
Sr _{0.95} Ce _{0.05} CoO _{3-x} Particles	0.05 mA cm ⁻²	1500 mAh g ⁻¹	250 mAh g ⁻¹	15 cycles at 0.2 mA cm ⁻²	S4
Sr ₂ CrMoO _{6-x} Particles	75 mA g ⁻¹	2306 mA h g ⁻¹ carbon	600 mAh g ⁻¹	30 cycles at 0.2 mA cm ⁻²	S5
LaNi _{1-x} Mg _x O ₃ Particles	-	620 mAh g ⁻¹	-	-	S6
LaNi _{1-x} Fe _x O ₃ Particles	50 mA g ⁻¹	500 mAh g ⁻¹ carbon	500 mAh g ⁻¹	10 cycles at 50 mA g ⁻¹	S7
Nano-sized La _{0.8} Sr _{0.2} MnO ₃ Particles	0.1 mA cm ⁻²	1922 mAh g ⁻¹ carbon	-	-	S8
Ketjen Black	0.025 mA cm ⁻²	3750 mAh g ⁻¹			This work
Super P	75 mA g ⁻¹	1434 mAh g ⁻¹			S5
XC-72	0.08 mA cm ⁻²	2454 mAh g ⁻¹			S9
Hierarchical Carbon-Nitrogen	50 mA g ⁻¹	3200 mAh g ⁻¹			S10
Ordered Mesoporous Carbon	200 mA g ⁻¹	3000-5500 mAh g ⁻¹			S11

References

(S1) Jin, C.; Yang, Z.; Cao, X.; Lu, F.; Yang, R. A Novel Bifunctional Catalyst of

Ba_{0.9}Co_{0.5}Fe_{0.4}Nb_{0.1}O_{3-δ} Perovskite for Lithium-Air Battery. *Int. J. Hydrogen*

Energy **2014**, 39, 2526-2530.

- (S2) Zhao, Y.; Xu, L.; Mai, L.; Han, C.; An, Q.; Xu, X.; Liu, X.; Zhang, Q. Hierarchical Mesoporous Perovskite $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{2.91}$ Nanowires with Ultrahigh Capacity for Li-Air Batteries. *Proc. Natl. Acad. Sci. U. S. A.* **2012**, 109, 19569-19574.
- (S3) Jung, K. N.; Lee, J. I.; Im, W. B.; Yoon, S.; Shin, K. H.; Lee, J. W. Promoting Li_2O_2 Oxidation by An $\text{La}_{1.7}\text{Ca}_{0.3}\text{Ni}_{0.75}\text{Cu}_{0.25}\text{O}_4$ Layered Perovskite in Lithium-Oxygen Batteries. *Chem. Commun.* **2012**, 48, 9406-9408.
- (S4) Yang, W.; Salim, J.; Li, S.; Sun, C.; Chen, L.; Goodenough, J. B.; Kim, Y. Perovskite $\text{Sr}_{0.95}\text{Ce}_{0.05}\text{CoO}_{3-\delta}$ Loaded with Copper Nanoparticles as A Bifunctional Catalyst for Lithium-Air Batteries. *J. Mater. Chem.* **2012**, 22, 18902-18907.
- (S5) Ma, Z.; Yuan, X.; Li, L.; Ma, Z. F. The Double Perovskite Oxide $\text{Sr}_2\text{CrMoO}_{6-\delta}$ as An Efficient Electrocatalyst for Rechargeable Lithium Air Batteries. *Chem. Commun.* **2014**, 50, 14855-14858
- (S6) Du, Z.; Yang, P.; Wang, L.; Lu, Y.; Goodenough, J. B.; Zhang, J.; Zhang, D. Electrocatalytic Performances of $\text{LaNi}_{1-x}\text{Mg}_x\text{O}_3$ Perovskite Oxides as Bi-functional Catalysts for Lithium Air Batteries. *J. Power Sources* **2014**, 265, 91-96.
- (S7) Zhang, D.; Song, Y.; Du, Z.; Wang, L.; Li, Y.; Goodenough, J. B. Active $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ Bifunctional Catalysts for Air Cathodes in Alkaline Media. *J. Mater. Chem. A* **2015**, 3, 9421-9426.

- (S8) Fu, Z.; Lin, X.; Huang, T.; Yu, A. Nano-sized $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ as Oxygen Reduction Catalyst in Nonaqueous Li/O_2 Batteries. *J. Solid State Electrochem.* **2012**, *16*, 1447-1452.
- (S9) Zhang, J.; Zhao, Y.; Zhao, X.; Liu, Z.; Chen, W. Porous Perovskite LaNiO_3 Nanocubes as Cathode Catalysts for $\text{Li}-\text{O}_2$ Batteries with Low Charge Potential. *Sci. Rep.* **2014**, *4*, 6005-6010.
- (S10) Zhang, Z.; Bao, J.; He, C.; Chen Y.; Wei, J.; Zhou, Z. Hierarchical Carbon-Nitrogen Architectures with Both Mesopores and Macrochannels as Excellent Cathodes for Rechargeable $\text{Li}-\text{O}_2$ Batteries. *Adv. Funct. Mater.* **2014**, *24*, 6826-6833
- (S11) Xie, J.; Yao, X.; Cheng, Q.; Madden, I. P.; Dornath, P.; Chang, C. C.; Fan, W.; Wang, D. Three Dimensionally Ordered Mesoporous Carbon as a Stable, High-Performance $\text{Li}-\text{O}_2$ Battery Cathode. *Angew. Chem. Int. Ed.* **2015**, *54*, 4299-4303.