

Supporting Information

Fabrication of ultra-stable composite electrode material of La₂O₃/Co₃O₄/graphene on nickel foam for high-performance supercapacitors

Zijing Wang,^a Shixiang Lu,^{*a} Wenguo Xu,^{*a} Ziwen Wang,^a and Hao Zuo,^a

School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing
100081, China.

**Corresponding author, E-mail: shixianglu@bit.edu.cn (Shixiang Lu); xuwg60@bit.edu.cn (Wenguo Xu)*

Experimental

S1: Preparation of CGN electrode material

0.6 mM (0.18 g) of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and 3.6 mM (0.216 g) of $\text{CH}_4\text{N}_2\text{O}$ were dissolved in 8 mL distilled water to obtain a homogeneous solution. The graphene solution (8 mL, 1 mg mL^{-1}) and the above solution were mixed and stirred vigorously for 0.5 h. The resulting solution with the cleaned NF was transferred to a 25 mL autoclave, heated at 120°C for 14 h, and then naturally cooled down to room temperature. Subsequently, the Co precursor/GO@NF sample was first fabricated, washed with ethanol and distilled water several times, then dried at 60°C for 8 h. Later, CGN was obtained after the Co precursor/GO@NF was annealed for 2 h at 300°C in a Muffle furnace. The mass of active substances grown on the CGN electrode is $\sim 1 \text{ mg cm}^{-2}$.

S2: Preparation of LGN electrode material

0.6 mM (0.195 g) of $\text{LaN}_3\text{O}_9 \cdot x\text{H}_2\text{O}$ and 3.6 mM (0.216 g) of $\text{CH}_4\text{N}_2\text{O}$ were dissolved in 8 mL distilled water to obtain a homogeneous solution. The graphene solution (8 mL, 1 mg mL^{-1}) and the above solution were mixed and stirred vigorously for 0.5 h. The resulting solution with the cleaned NF was transferred to a 25 mL autoclave, heated at 120°C for 14 h, and then naturally cooled down to room temperature. Subsequently, the La precursor/GO@NF sample was first fabricated, washed with ethanol and distilled water several times, then dried at 60°C for 8 h. Later, LGN was obtained after the La precursor/GO@NF was annealed for 2 h at 300°C in a Muffle furnace. The mass of active substances grown on the LGN electrode is $\sim 1 \text{ mg cm}^{-2}$.

S3: Preparation of LCN electrode material

0.6 mM (0.18 g) of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and 0.6 mM (0.195 g) of $\text{LaN}_3\text{O}_9 \cdot x\text{H}_2\text{O}$ were dissolved in 8 mL distilled water to obtain a homogeneous solution. The graphene solution (8 mL, 1 mg mL^{-1}) and the above solution were mixed and stirred vigorously for 0.5 h. The resulting solution with the cleaned NF was transferred to a 25 mL autoclave, heated at 120°C for 14 h, and then naturally cooled down to room temperature. Subsequently, the sample of La-Co precursor @NF was first fabricated, and washed with ethanol and distilled water several times, then dried at 60°C for 8 h. Later, LCN was obtained after the La-Co precursor @NF was annealed for 2 h at 300°C in a Muffle furnace. The mass of active substances grown on the LCN electrode is $\sim 1 \text{ mg cm}^{-2}$.

S4: Preparation of GN electrode material

The graphene solution (16 mL , 2 mg mL^{-1}) was stirred vigorously for 0.5 h. Then the solution with the cleaned NF was transferred to a 25 mL autoclave, heated at 120°C for 14 h, and then naturally cooled down to room temperature. Subsequently, the sample of GO@NF was first fabricated, and washed with ethanol and distilled water several times, then dried at 60°C for 8 h. Later, GN was obtained after the GO@NF was annealed for 2 h at 300°C in a Muffle furnace. The mass of active substances grown on the GN electrode is $\sim 1 \text{ mg cm}^{-2}$.

Results and discussion

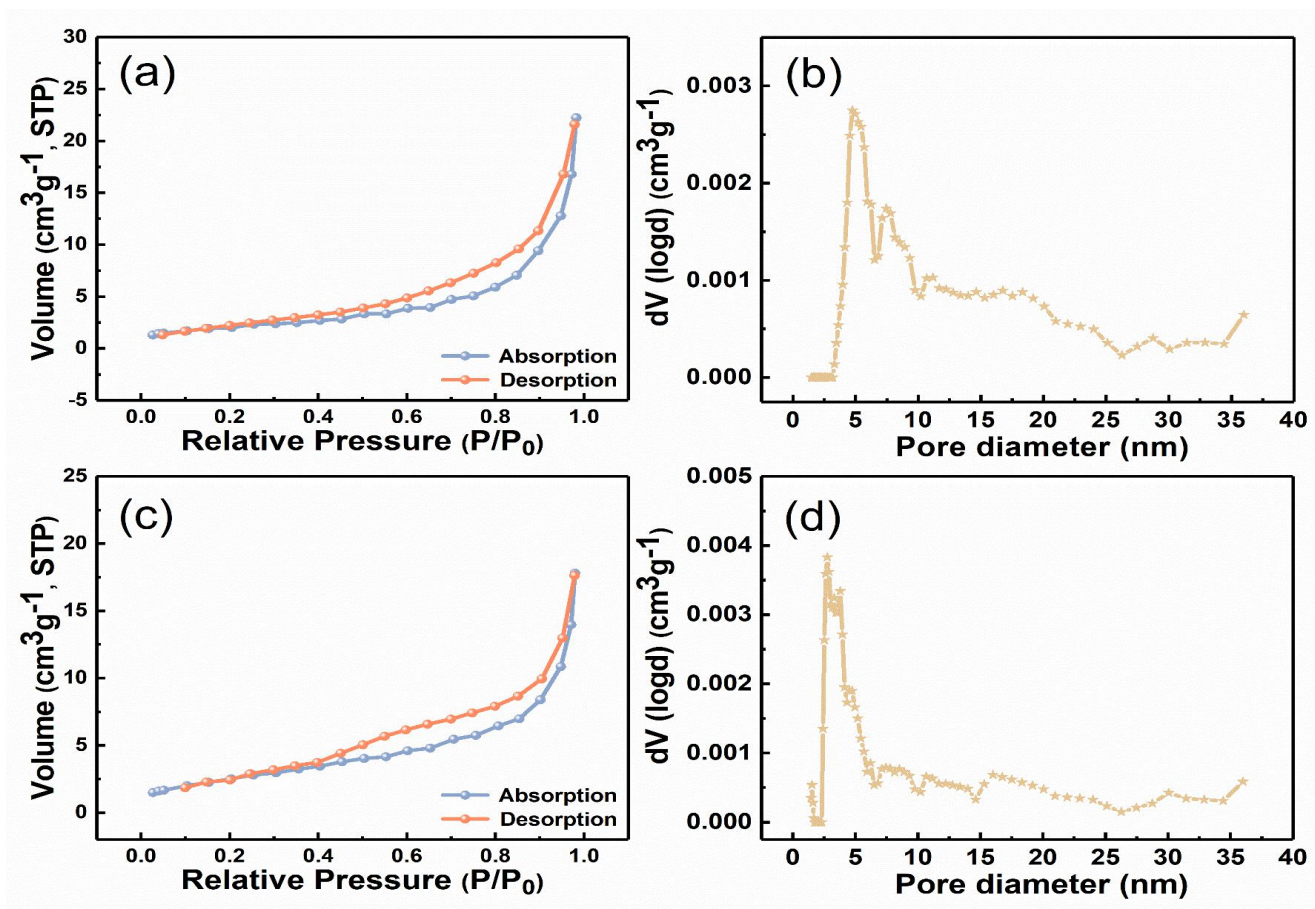


Fig. S1. (a) N₂ adsorption-desorption isotherm of LGN and (b) the corresponding pore size distribution of LGN; (c) N₂ adsorption-desorption isotherm of CGN and (d) the corresponding pore size distribution of CGN.

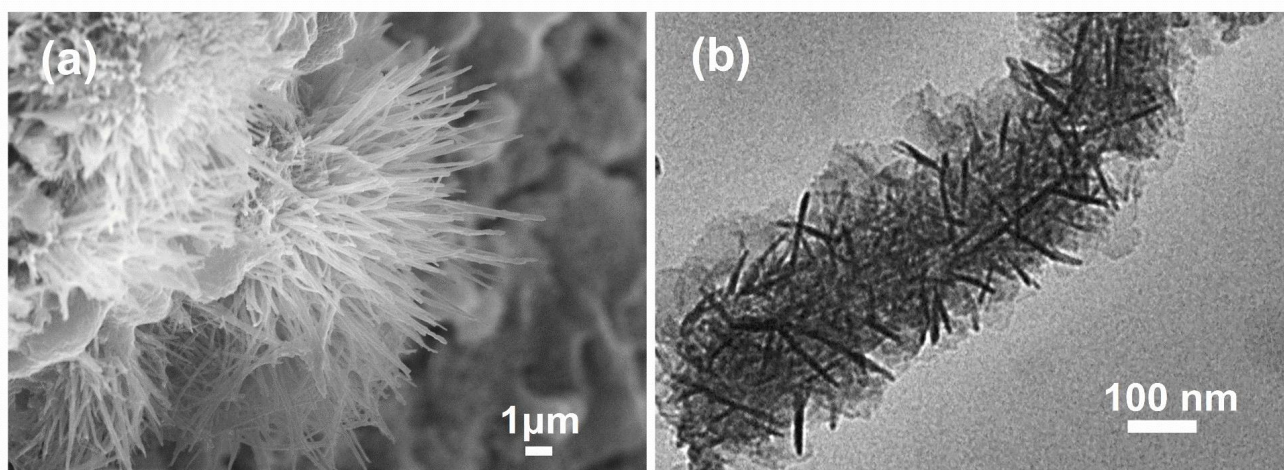


Fig. S2. (a) SEM image of CGN and (b) TEM image of CGN;

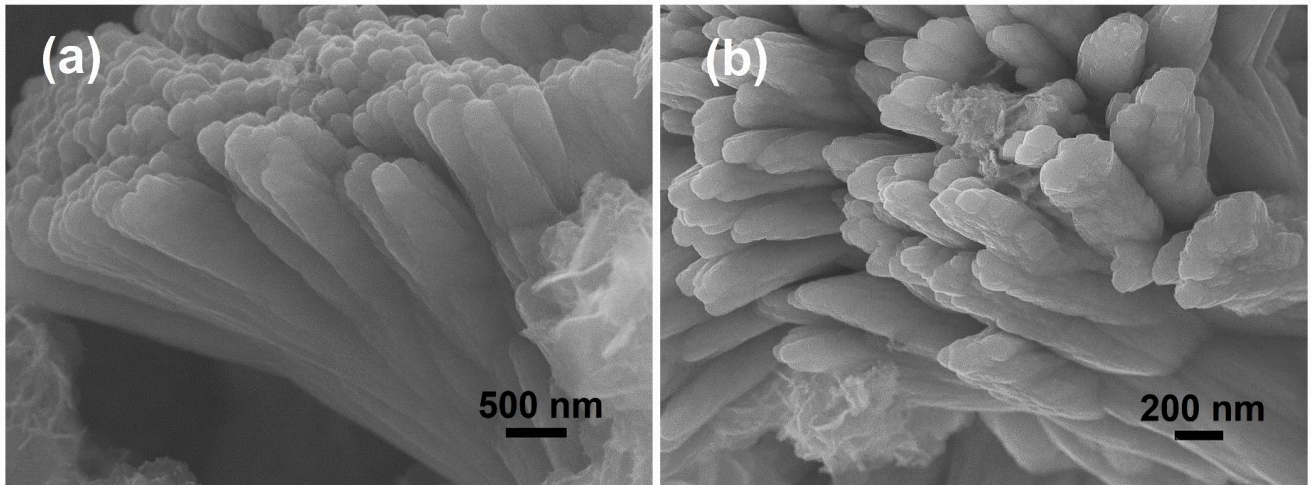


Fig. S3. (a) and (b) SEM images with different magnification of LGN.

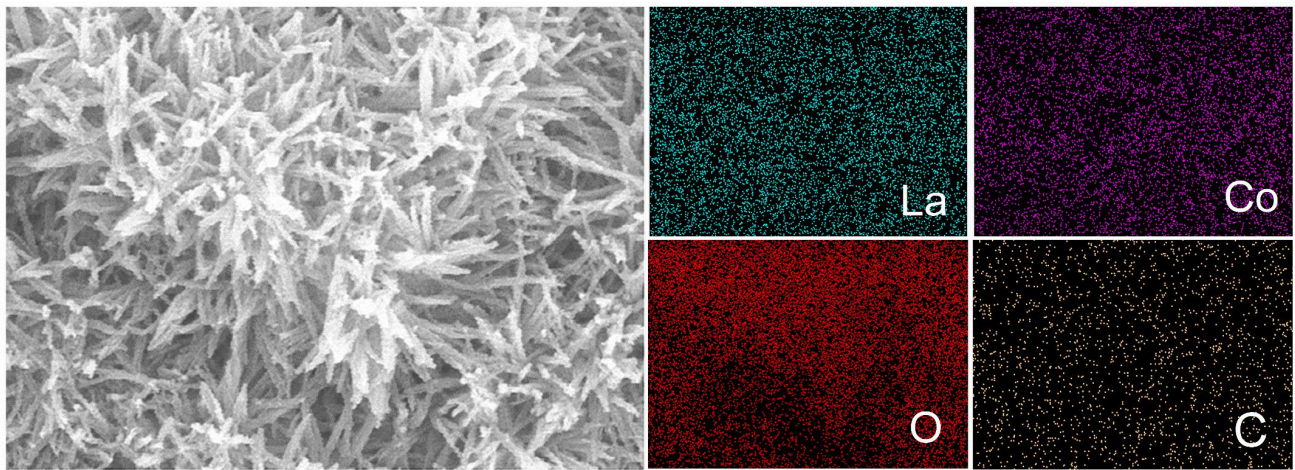


Fig. S4. EDS elemental mapping images of the composite (La, Co, O and C).

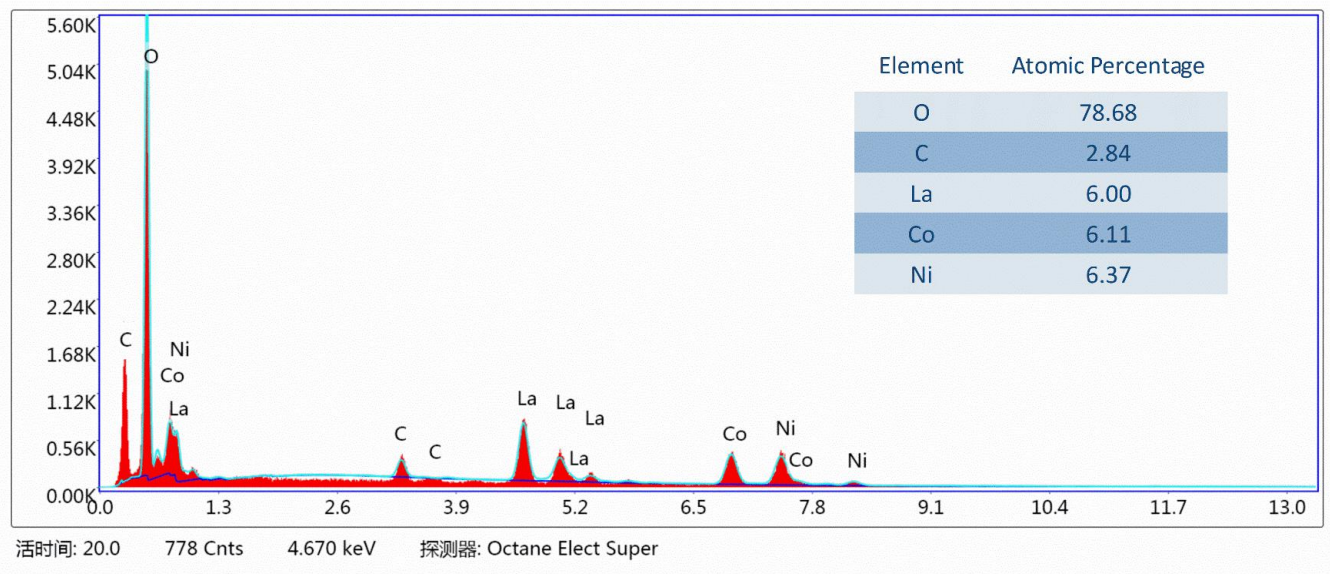


Fig. S5. EDS elemental mapping images of LCGN.

Table S1 Comparison of electrochemical performances of LCGN electrode in our work with previous.

Materials	Specific capacitance	capacitance retention (%)	Stability (%)	Current density	Refs.
Co ₃ O ₄ composites	1455.64 F g ⁻¹ at 1.0 A g ⁻¹ in 6 mol L ⁻¹ KOH	88% (0.5 to 20 A g ⁻¹)	82.52% (2000 cycles)	5 A g ⁻¹	1
Co ₃ O ₄ / flocculent graphene composites	1584F g ⁻¹ at 1.0 A g ⁻¹ in 5 mol L ⁻¹ KOH	63.89% (1 to 6.5 A g ⁻¹)	90% (800 cycles)	10 A g ⁻¹	2
ZnO / Co ₃ O ₄ composites	1135 F g ⁻¹ at 1.0 A g ⁻¹ in 1 mol L ⁻¹ KOH	42% (1 to 10 A g ⁻¹)	83% (5000 cycles)	10 A g ⁻¹	3
Co ₃ O ₄ / MnO ₂ CC composites	616.7 F g ⁻¹ at 2.0 A g ⁻¹ in 1 mol L ⁻¹ Na ₂ SO ₄	77.6% (2 to 20 A g ⁻¹)	86.3% (10000cycles)	2 A g ⁻¹	4
MnO ₂ / La ₂ O ₃	1696 F g ⁻¹ at 1.0 A g ⁻¹ in 0.5 mol L ⁻¹ Na ₂ SO ₄	58.6% (1 to 15 A g ⁻¹)	88% (2000 cycles)	5 A g ⁻¹	5
La ₂ O ₃ / rGO composites	156.25 F g ⁻¹ at 0.1 A g ⁻¹ in 3 mol L ⁻¹ KOH	66.67% (0.1 to 0.5 A g ⁻¹)	78% (500 cycles)	0.1 A g ⁻¹	6
La ₂ O ₃ / Co ₃ O ₄ / G composites	2945.11 F g ⁻¹ at 1 A g ⁻¹ in 6 mol L ⁻¹ KOH	79.2% (1 to 30 A g ⁻¹)	96% (30000 cycles)	1 A g ⁻¹	This work

References

1. A. Umar, S. D. Raut, A. A. Ibrahim, H. Algadi, H. Albargi, M. A. Alsaiari, M. S. Akhtar, M. Qamar and S. Baskoutas, *Electrochimica Acta*, 2021, **389**.
2. C. H. Wu, Q. Shen, R. Mi, S. X. Deng, and H. Yan, *Journal of Materials Chemistry A*, 2014, **2**, 15987-15994.
3. M. Gao, W. K. Wang, Q. Rong, J. Jiang, Y. J. Zhang and H. Q. Yu, *ACS Appl Mater Interfaces*, 2018, **10**, 23163-23173.
4. G. Liu, L. Ma and Q. Liu, *Electrochimica Acta*, 2020, **364**, 137265.
5. C. Sun, W. Pan, D. Zheng, R. Yao, and D. Jia, *Energy & Fuels*, 2020, **34**, 14882-14892.
6. J. Zhang, Z. Zhang, Y. Jiao, H. Yang, Y. Li, J. Zhang and P. Gao, *Journal of Power Sources*, 2019, **419**, 99-105.