Facile Growth of binder-free Co$_3$O$_4$@FNF electrode with superior electrochemical performance for energy storage and sensing applications

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1. **Symmetric and asymmetric devices testing:**

In symmetric devices, both electrodes consist of identical materials (Co_3O_4@FNF-1), resulting in balanced charge storage and discharge cycles Fig. S1a. While this symmetry provides stability, it limits the overall energy storage capacity and the amount of current the device can supply. This typically leads to a lower power output and a dimmer glow in the LED Fig. S1b. In contrast, asymmetric devices, which use different materials for the positive and negative electrodes, leverage the unique properties of each material. For example, one electrode may offer high energy density (Co_3O_4@FNF-1), while the other provides high power density (carbon foam) Fig. S1c. This complementary combination allows the asymmetric device to store and deliver more energy, resulting in a higher current being supplied to the LED and thus a brighter glow Fig. S1d.

The increased energy density in asymmetric devices plays a critical role in delivering more charge at a given voltage, leading to a higher power output. According to basic electrochemical principles, the power delivered to an external load (such as an LED) is proportional to the current, and devices that can generate higher current will naturally deliver more power, producing brighter illumination. Furthermore, asymmetric electrode configurations can often operate over a wider voltage window compared to symmetric devices. Different materials used in each electrode allow the device to function at a broader range of potentials, which increases the overall energy delivered during discharge, contributing to the enhanced brightness of the LED.[1]

In addition to energy density, the efficiency of electron and ion transport in asymmetric devices is a key factor in their superior performance. The use of different materials enhances charge transfer kinetics, facilitating more efficient electron flow at the electrode-electrolyte interface. This faster charge transfer improves the device's ability to deliver higher currents, resulting in increased power output and, consequently, a brighter LED. In symmetric devices, the identical materials used for both electrodes limit this charge transfer efficiency, leading to a lower current supply and reduced LED brightness.[2]

Another factor contributing to the superior performance of asymmetric devices is their charge-discharge behavior. Asymmetric devices tend to exhibit slower energy decay during discharge, meaning they can sustain higher currents over longer periods. This sustained energy output enables the LED connected to the asymmetric device to maintain its brightness for a more extended time compared to the symmetric device. The ability of the asymmetric configuration to deliver more energy efficiently over time, along with a higher energy density and broader operating voltage, makes it a more effective power source for applications like LED lighting.[3]

The observed difference in LED brightness between symmetric and asymmetric devices is rooted in the superior energy storage, charge transfer efficiency, and discharge behavior of the asymmetric configuration. By combining materials with complementary properties, asymmetric devices can deliver more power and sustain energy output over a longer period, making them more suitable for high-performance applications where both energy density and power output are crucial.
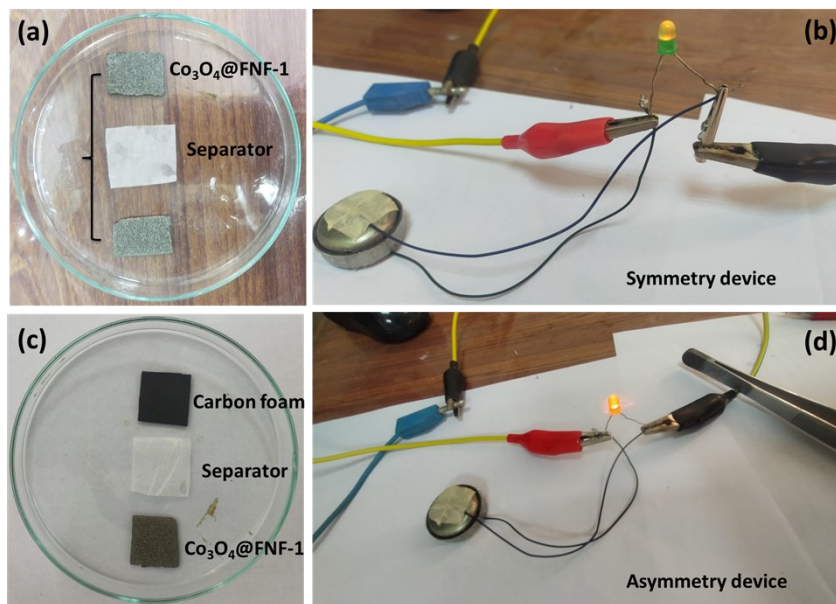

Fig. S1. A digital photograph of a light-emitting diode (LED) powered by a two-electrode type of (a,b) symmetry supercapacitor device; (c,d) asymmetry supercapacitor device.

Table S1: A comparison of Co_3O_4-based supercapacitor electrodes reported in the previous literature.

Electrode material	Electrolyte	Specific capacitance F/g	Current density A/g	Cycling stability	Ref
Cobalt-nickel oxide	2 M KOH	267	0.5	8% 2500 cycles	[4]
Cobalt oxide	1M KOH	954	1	88% 2000 cycles	[5]
3D-carbon fiber network anchored with Co metal	2 M KOH	762	1	94.5% 5000 cycles	[6]
Manganese-cobalt oxide	2 M KOH	852	12	92.9% 4000 cycles	[7]
Hierarchical nanostructure of Co_3O_4	5 M KOH	1273	1	96% 5000 cycles	[8]
9 wt% Zr-doped ZnO	1 M KOH	518	1	94% 5000 cycles	[9]
$Ce_{1-x}Ni_xO_2(x = 0.1)$	....	446	...	97 % 2000 cycles	[10]
9 wt% Cd-doped ZnO	....	627	1	93.3 % 5000 cycles	[11]
9 wt% Sr-doped ZnO	1 M KOH	698	1	95.4 5000 cycles	[12]
Ultrafine cobalt oxide nanoparticles	6 M KOH	523.0	0.5	104.9% 1500 cycles	[13]
Co_3O_4@FNF-1	**6 M KOH**	**1433**	**0.5**	**96 % 8000 cycles**	**Present work**

2. Graph comparing the GCD curves for the first and last few cycles:

The slight decrease in specific capacitance from 3.36 F/g in the first cycle to 3.17 F/g in the last cycle during the long cycle test likely results from minor degradation of the electrode material, such as surface morphology or structural changes, which can reduce the active surface area. Additionally, the formation of a solid-electrolyte interface (SEI) layer can increase charge-transfer resistance, and ion diffusion pathways may become less efficient, both contributing to the slight drop in capacitance. Despite these factors, the minimal decrease indicates good overall stability of the electrode material.
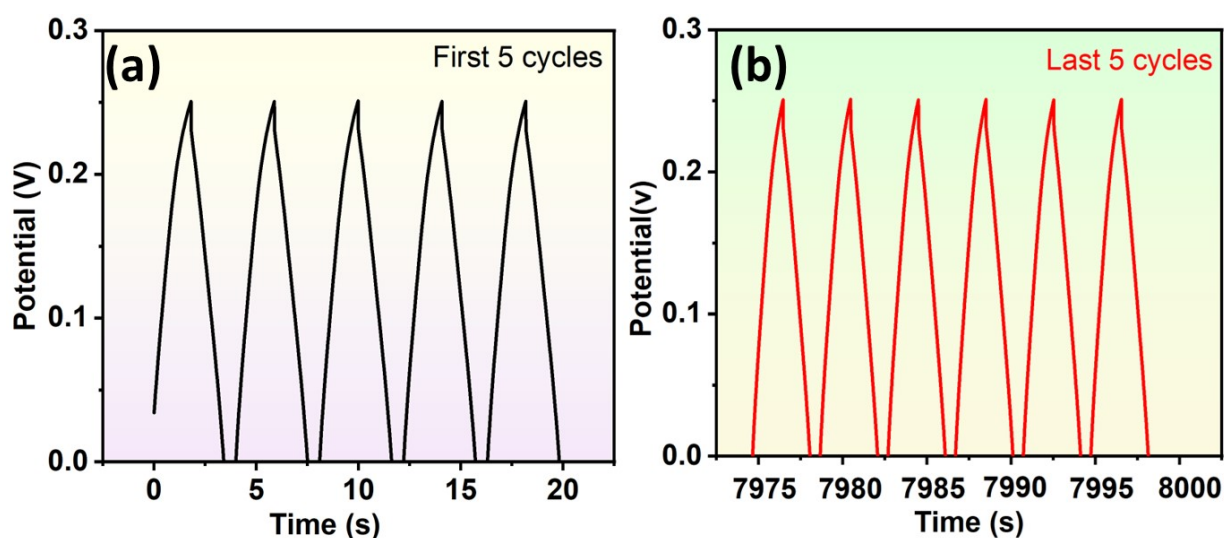

Fig. S2. Comparing the GCD curves (a) first five cycles; (b) last five cycles.

References

1   Y. Liu, Y. Shi and X. Xu, *Energy Storage Materials*, 2021, **41**, 677–696.

2   M. Z. Iqbal, S. S. Haider, S. Siddique, M. R. A. Karim, S. Zakar, M. Tayyab, M. M. Faisal, M. Sulman, A. Khan, M. Baghayeri, M. A. Kamran, T. Alherbi, M. J. Iqbal and T. Hussain, *Journal of Energy Storage*, 2020, **27**, 101056.

3   Y. Gao and L. Zhao, *Chemical Engineering Journal*, 2022, **430**, 132745.

4   Z. Zeng, B. Xiao, X. Zhu, J. Zhu, D. Xiao and J. Zhu, *Ceramics International*, 2017, **43**, S633–S638.

5   L. Kunhikrishnan and R. Shanmugham, *Materials Characterization*, 2021, **177**, 111160.

6   A. P. Tiwari, S.-H. Chae, G. P. Ojha, B. Dahal, T. Mukhiya, M. Lee, K. Chhetri, T. Kim and H.-Y. Kim, *Journal of Colloid and Interface Science*, 2019, **553**, 622–630.

7   H.-J. Kim, B. Naresh, I.-H. Cho, J.-S. Bak, S. A. Hira, P. R. Sekhar Reddy, T. N. V. Krishna, K. Dasha Kumar, B. A. Mola and Y. A. Kumar, *Journal of Energy Storage*, 2021, **40**, 102702.

8   E. A. A. Aboelazm, G. A. M. Ali, H. Algarni, H. Yin, Y. L. Zhong and K. F. Chong, *The Journal of Physical Chemistry C*, 2018, **122**, 12200–12206.

9   M. D. Angelin, S. Rajkumar, J. P. Merlin, A. R. Xavier, M. Franklin and A. T. Ravichandran, *Ionics*, 2020, **26**, 5757–5772.

10   J. Alex, S. Rajkumar, J. PrincyMerlin, A. Aravind, D. Sajan and C. S. Praveen, *Journal of Alloys and Compounds*, 2021, **882**, 160409.

11   M. D. Angelin, S. Rajkumar, A. T. Ravichandran and J. P. Merlin, *Journal of Physics and Chemistry of Solids*, 2022, **161**, 110486.

12   M. D. Angelin, S. Rajkumar, S. Dhineshkumar, A. T. Ravichandran, A. Ravikumar and J. P. Merlin, *Journal of Materials Science: Materials in Electronics*, 2023, **34**, 1107.

13   F. Liu, H. Su, L. Jin, H. Zhang, X. Chu and W. Yang, *Journal of Colloid and Interface Science*, 2017, **505**, 796–804.