

Construction Of High Energy Density and Long Cycle Life Zinc-ion Hybrid Capacitors Based on Wedelia Chinensis-Derived Biomass Porous Carbon

Miaomiao Liu

Lanzhou University of Technology

Shenteng Wan

Lanzhou University of Technology

Letong Wang

Lanzhou University of Technology

Zengwei Pang

Lanzhou University of Technology

Tong Yao

Lanzhou University of Technology

xiaohui niu

Lanzhou University of Technology

Kunjie Wang

Lanzhou University of Technology

Hongxia Li

lhxwkj790425@lut.edu.cn

Lanzhou University of Technology

Research Article

Keywords: Zinc ion hybrid capacitor, Capacitive materials, Biomass-derived porous carbon, Wedelia chinensis, Energy storage

Posted Date: August 26th, 2024

DOI: <https://doi.org/10.21203/rs.3.rs-4810494/v1>

License:   This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Additional Declarations: No competing interests reported.

Abstract

Zinc ion hybrid capacitors (ZIHCs) have received much attention due to their low cost, safety and green features. However, its development is seriously restricted by defects such as low energy density and insufficient cycle life. The selection of suitable capacitive materials can effectively enhance their electrochemical performance. Porous carbon materials become the choice of capacitive materials for ZIHCs due to their high ion adsorption capacity and fast kinetic behavior. In this paper, an oxygen-enriched biomass-derived nanoporous carbon was prepared by pyrolysis of *Wedelia chinensis* combining the chemical activation. The oxygen-rich functional groups on the surface of this nanoporous carbon can provide additional pseudocapacitance and improve the wettability of the material. The excellent electrochemical performance of the material in aqueous electrolyte was verified by assembling symmetrical capacitors (SCs) and ZIHCs devices. Specifically, as high as 151 W h kg^{-1} of energy density and 18 kW kg^{-1} of power output as well as 25000 cycles of long cycle life with 97.4% of capacity retention were demonstrated by as-assembled ZIHC.

1. Introduction

Due to the growing demand for green energy, different application scenarios have arisen, including rechargeable ion batteries with high energy density but low power density and short cycle life, and supercapacitors with high power density and long cycle life but low energy density.[1–3] Metal-ion hybrid capacitors (MIHCs), integrating the features of high energy density and power supplying, have become the focus of research on the next generation of energy storage devices.[4–7] Among them, zinc ion hybrid capacitors (ZIHCs) have been focused due to the higher theoretical capacity of zinc metal anode (823 mAh g^{-1} or 5851 mAh cm^{-3}), low redox potential (-0.76 V vs. standard hydrogen electrode), stability in air atmosphere, low cost, and good biocompatibility.[8–10]

Excellent capacitive materials are an important part of ZIHCs, it can effectively improve the power density and cycle stability of ZIHCs.[11, 12] Among which activated carbon (AC) is a more mature capacitive electrode, but the energy storage performance of commercial AC is poor (energy density and power density are only 43.1 Wh kg^{-1} and 12.0 kW kg^{-1}).[13, 14] The energy storage performance of porous carbon is related to the specific surface area, pore structure and heteroatom doping.[15] Therefore, the preparation of new porous carbon with enhanced energy storage performance is an important mean to improve the electrochemical performance of ZIHCs.[16, 17]

In this paper, *Wedelia chinensis* was used as a biomass carbon source. We systematically investigated the effect of activation ratio on the specific surface area, pore structure and oxygen-containing functional groups on the surface of the materials and optimized the preparation conditions to prepare biomass-derived carbon materials (Fig. 1). The as-prepared *Wedelia chinensis*-derived biomass nanoporous activated carbon (WPAC) material showed high specific capacity (335.9 F g^{-1}), excellent rate performance and good cycling stability (after 25000 cycles at the current density of 10 A g^{-1} , 97.4% of capacity retention is remained) in zinc ion hybrid capacitors.

2. Experimental Section

2.1 Preparation of WPAC

Wedelia chinensis was washed with distilled water and anhydrous ethanol several times to remove the surface dust, dried and then crushed and ground to powder. The powder was pre-carbonized by annealing at 600°C under Ar gas atmosphere for 2 h. After that, the pre-carbonized product and KOH were mixed thoroughly with different mass ratios. The mixture was transferred to a tube furnace and annealed under Ar gas atmosphere at 800°C for 2 h with a heating rate of 5 °C/min. The annealed product was washed several times with 1 M HCl, then washed thoroughly with distilled water to neutral. After dried at 100°C for 12 h, the obtained *Wedelia chinensis*-derived nanoporous activated carbon were denoted as WPAC-X (X meant mass ratio of KOH).

2.2 Materials characterization

The morphological characteristics of the materials were observed using scanning electron microscopy (SEM, JEOL, JSM-6701F, Japan) and transmission electron microscopy (TEM, JEOL JEM-2100FEG, Japan). The physical phase of the samples was characterized using an X-ray diffractometer (XRD, X'Pert Pro, Netherlands). The surface elemental study of the samples was performed using monochromatic Al-K α radiation (1486.6 eV) X-ray photoelectron spectroscopy (XPS, scalab250Xi). Raman spectrum analysis was carried out on Raman microscope. Nitrogen adsorption/desorption isotherms were tested at 77 K on a Micromeritics ASAP 2020 Volumetric Adsorption Analyzer to determine the specific surface area and pore size distribution of the materials.

2.3 Electrochemical measurement

The active material, acetylene black and polytetrafluoroethylene (PTFE) binder were mixed with the mass ratio of 8:1:1 in deionized water, making a uniform slurry. The slurry was evenly pasted on nickel foam (1 cm $\times$ 1 cm or D1.2 cm, for supercapacitor) or steel mesh (D1.2 cm for ZIHCs) and dried at 60°C for 12 h. Before assemble of the devices, the dried electrodes were pressed using a pressure of 8 MPa.

The electrochemical performance in 2 M KOH was studied firstly in three-electrode system. The saturated calomel electrode and the Pt foil electrode were used as reference and counter electrodes. The PP/PE membrane served as the separator to build the CR2032 type coin cell for symmetrical supercapacitors. As for ZIHCs, the polished zinc foils were used as the anode, the WPAC as the cathode, the glass fibers (Whatman, GF/D) as separator, a series of CR2032 coin-type ZIHCs devices were built in 2 M Zn(CF₃SO₃)₂. [18]

3. Results and Discussion

3.1 Morphology and Structural Feature of WPAC-X

According to the experimental procedure, we successfully prepared three biomass-derived carbons: WPAC-2, WPAC-3, and WPAC-4. SEM reveals that all three samples exhibit a folded floral stacking morphology (Fig. 2a, Figure S1a-b). The surface of the materials has a relatively abundant pores structure, which is formed by the etching of KOH at high temperature (Fig. 2b). This structure facilitates the penetration and conduction of the electrolyte, which is favorable for ion transport and charge transfer.[19] As shown in the HRTEM and SAED images, the prepared nanoporous carbon materials display an amorphous structure (Fig. 2b-c).[20] As shown in the XRD pattern, WPAC-X has two diffraction peaks at 23° and 44° , corresponding to the (002) and (101) crystal planes of the graphite structure. The disappearance of the diffraction peak of WPAC-3 at 44° suggests that it has a more amorphous structure (Fig. 2d).[21] The intensity of peak decreases with the increase of the activation ratio, indicating more defect and lower graphitization degree are formed in materials.[22] The two broad peaks centered at 1360 and 1568 cm^{-1} correspond to the known D- and G-bands, respectively. The intensity ratios of ID/IG are $0.98\text{--}1.45$, further demonstrating the amorphous structure of WPAC-X.[23] The pore structure of the materials is investigated by the N_2 adsorption and desorption isotherms. As shown in Fig. 2f, all samples showed typical I-type nitrogen adsorption and desorption isotherms. The higher nitrogen adsorption in the low relative pressure of $P/P_0 < 0.05$ indicates that there were a large number of micropore structures in the WPAC-X material.[24] Among them, the nitrogen adsorption of WPAC-3 was higher than that of the other two samples, indicating that a larger specific surface area (SSA) was produced after KOH activation. As shown in Table S1, the SSA and pore volume of the products increased significantly with the increase of the activation ratio. However, when the activation ratio was further increased to 1:4, the SSA and pore volume of the products began to decrease, signifying that the structure might collapse due to the over-etching by potassium hydroxide. Therefore, the highest pore volume ($0.96\text{ cm}^3\text{ g}^{-1}$) and SSA ($2215.4\text{ m}^2\text{ g}^{-1}$) were held by WPAC-3. The abundant micropore structure and large pore volume can provide a higher SSA, which will provide more active sites to improve the kinetic behavior and energy storage performance of the material.

The elemental composition of the WPAC-X was analyzed using X-ray photoelectron spectroscopy (XPS). The full spectra of WPAC-X showed two sharp peaks at 284.8 and 532.7 eV , corresponding to C 1s and O 1s. This indicates that the surface and near-surface of the carbon material only contains carbon and oxygen two elements. Furthermore, the oxygen content increases with increasing activation degree.[25] Table S2 shows that the highest oxygen content of the sample is $7.21\text{ at\%}$ when the activation ratio is 1:4. The oxygen content is $6.85\text{ at\%}$ and $6.45\text{ at\%}$ when the activation ratio is 1:2 and 1:3, respectively. As the activation ratio increases, the degree of activation increases, resulting in a higher degree of KOH etching on the carbon skeleton. This leads to the production of more defects, oxygen-containing functional groups, and a decrease in the degree of graphitization of the samples. Although the WPAC-3 sample has the lowest oxygen content on or near the surface, it is expected to have more accessible oxygen-containing functional groups exposed to the electrolyte due to its larger specific surface area. These structural differences are likely to be the main reason for the differences in their electrochemical properties. Regarding the WPAC-3 samples, the high resolution C1s spectra display four peaks corresponding to C-C (284.2 eV), C = C (284.7 eV), C = O (286.3 eV) and COOR (288.9 eV), respectively

(Fig. 2h). The O 1s spectrum can be deconvoluted into three peaks at 532.1, 533.2 and 534.5 eV, which belong to O = C, O-C and O = C-O, respectively (Fig. 2i). The oxygen-containing functional groups is conducive to boosting the pseudocapacitive contribution and improving the wettability of the electrode material.[26]

3.2 Electrochemical Performance of WPAC-X in 2M KOH

To evaluate the electrochemical performance and optimize the activation conditions of WPAC-X, a three electrode system was assembled in 2 M KOH by using Pt and HgO electrodes as the counter and reference electrodes. The CV curves of WPAC-X are quasi-rectangular at scan rates ranging from 10 to 200 mV^{-1} , indicating a typical electric double-layer capacitance (EDLC) energy storage mechanism (Fig. 3b and Figure S3a, c). The symmetrical triangle shape of GCD plots of three samples signifies a high reversibility and Coulombic efficiency (CE) in the energy storage process (Fig. 3c and Figure S3b,d). However, the WPAC-3 has the largest integral area in the CV curves and the longest discharge time in the GCD plots, showing optimal electrochemical performance among three samples (Fig. 3a). Additionally, the Nyquist plots indicate that WPAC-3 has the lowest charge transfer resistance in the high frequency region, suggesting superior ion transport performance compared to WPAC-2 and WPAC-4. Furthermore, the WPAC-3 electrode material exhibits exceptional cycling performance, retaining 92.1% of its initial capacity after 10,000 cycles at 10 A g^{-1} .

To validate the advantages of WPAC-3 in electrochemical performance, a symmetrical capacitor (SC) with 2 M KOH as the electrolyte was constructed. The CV curves show that all WPAC-X-based symmetric capacitors (SCs) exhibit a quasi-rectangular shape, but WPAC-3-based SC has a largest integral area of CV curve (Fig. 4a and Figure S3a, c). Furthermore, the GCD result also shows that the WPAC-3-based SC has the highest specific capacitance at the all current densities ranging from 1 to 20 A g^{-1} (Fig. 4b, c). The CV curves of WPAC-X exhibit no significant deformation at different scanning speeds, indicating good reversibility (Fig. 4d, Figure S4a, c). Although WPAC-3-based symmetric supercapacitors do not exhibit the highest specific capacitance at small current densities (Fig. 4c), they have the slowest capacitance decay rate and the best rate performance as the current density increases (with an initial capacity retention rate of 62.5% for a 40-fold increase in current density). The GCD curve shows no obvious IR drop when the current density is lower than 10 A g^{-1} . At a current density of 20 A g^{-1} , a slight IR drop is observed, indicating the excellent conductivity of WPAC-3 (Fig. 4e, Figure S4b, d).[27] The SC based on WPAC-3 exhibits a maximum energy density of 9.79 W h kg^{-1} at a power output of 250 W kg^{-1} (Fig. 4f). Additionally, it demonstrates good cycle stability with high CE, maintaining nearly 100% of capacitance retention after 20,000 cycles at a high current density of 5 A g^{-1} (Fig. 4g).

The experimental results indicate that the WPAC-3 electrode material exhibits the optimal electrochemical performance among three samples. The performance is closely related with the structural features of material. The superior rate capability and high specific capacitance of WPAC-3 can be ascribed to its high SSA, abundant pore structure and ample oxygen-containing functional groups. However, limiting by the energy storage mechanism of EDLC, the overall performance of SCs, especially

the energy density, is still far below the consumer demands. Introducing a battery-type material as anode to supply high energy density, a capacitor-type material as cathode to guarantee the power outputting, an advanced metal ion hybrid capacitor can be constructed to achieve high energy-power and long cycle life.

3.3 Electrochemical Performance of WPAC-3 in ZIHCs

Hence, a zinc ions hybrid capacitor was constructed by using Zn metal as the anode, WPAC-3 as cathode material, 2 M zinc trifluoromethanesulfonate as the electrolyte. Figure 5a shows that the ZIHC exhibits a CV curve that differs from both the capacitor and battery systems in the voltage range of 0 ~ 1.8 V. This is due to the presence of two distinct energy storage mechanisms. The GCD curve also differs significantly from the electric double-layer capacitor, exhibiting a slightly distorted triangular shape (Fig. 5b). However, no significant IR drop is observed at different current densities, indicating good conductivity and reversibility of the electrode material in electrochemical energy storage.[28] Fig. 5c shows the results of calculating the specific capacity of the device at different current densities. At a current density of 0.5 A g^{-1} , the device achieves a high specific capacity of 335.9 F g^{-1} . At a current density of 20 A g^{-1} , the specific capacity is 185 F g^{-1} , which is 55.1% of the initial capacity, demonstrating excellent rate performance. The Zn//WPAC-3 ZIHC device achieves a high energy density and high power density due to the combination of two energy storage mechanisms and the superior performance of our synthesized electrode materials. At a power density of 450 W kg^{-1} , it achieves a maximum energy density of $151.3 \text{ W h kg}^{-1}$. Even at a high power density of 18 kW kg^{-1} , it can still achieve an energy density of 82.5 W h kg^{-1} . The performance of the Zn//WPAC-3 ZIHC is superior to that of the recently reported ZIHC, as shown in Fig. 5d.[2, 5, 17, 29] We investigated the cycling stability of the Zn//WPAC-3 ZIHC at a current of 10 A g^{-1} . After 25,000 cycles, the capacity retention of the Zn//WPAC-3 ZIHC remained at 97.4%, indicating excellent cycling stability, as shown in Fig. 5e. Furthermore, the Zn//WPAC-3 ZIHC device can power a “LUT” logo comprising 20 red bulbs in parallel (inset of Fig. 5e), demonstrating its practical application potential.

To specifically analyze the kinetic behavior of the energy storage process, the CV curves were further analyzed according to the equation:

$$i = ab^v [30] (1)$$

The b values at different voltages were obtained (Fig. 5f). Obviously, at a voltage range of 0.7–1.7 V, the b value was above 0.9. The energy storage was mainly contributed by the capacitive behavior. Closing to lower or higher voltage range, the b value fluctuated between 0.76 and 0.81, indicating that the diffusion controlled process was enhanced. The contribution of diffusion-controlled process ($k_2v^{1/2}$) and capacitive behavior (k_1v) could be distinguished quantitatively by the equation:

$$i = k_1v + k_2v^{1/2} [30] (2)$$

The contribution ratios of capacitive behavior increased from 71.7–95.3% when the scan rates increased from 5 to 50 mV s⁻¹ (Fig. 5g-h). This proves that the capacitive behavior is dominant in the energy storage process, which is conducive to the realization of high-performance ZIHs with high rate capability and power characteristics.

4. Conclusion

In summary, a high-performance aqueous zinc ion hybrid capacitor was constructed using *Wedelia chinensis*-derived biomass nanoporous carbon (WPAC-3) as a capacitor electrode. The advanced WPAC-3 was prepared using biomass as the raw material and high-temperature activation, resulting in a porous structure that enhances the contact area of electrolyte ions. Compared to commercial activated carbon (C-AC), this material exhibits significantly improved kinetics and energy storage performance.

Additionally, the oxygen-containing functional groups on its surface promote the chemisorption of Zn²⁺ at the electrode. The Zn//Zn(CF₃SO₃)₂//WPAC-3 zinc-ion hybrid capacitor demonstrated a high specific capacity of 335.9 F g⁻¹ at 0.5 A g⁻¹ (corresponding to 151 Wh kg⁻¹ of energy density) and maintained long-term cycling stability at a high power output of 18 kW kg⁻¹. After 25,000 cycles at 10 A g⁻¹, 97.4% of the initial capacity was retained. This study provides new insights into surface engineering strategies for electrode materials preparation.

Declarations

Conflicts of Interest

No conflict of interest exists in the submission of this manuscript.

Author Contribution

Miaomiao Liu: Investigation, Data curation, Formal analysis, Writing-original draft
Shenteng Wan: Investigation, Data curation, Formal analysis, Writing-original draft
Letong Wang: Experimental verification, syntax checking
Zengwei Pang: Formal analysis, syntax checking
Tong Yao: Investigation, Formal analysis
Xiaohui Niu: Supervision
Kunjie Wang: Conceptualization, Supervision, Funding acquisition, Project administration
Hongxia Li: Conceptualization, Supervision, Funding acquisition, Project administration

Acknowledgements

Miaomiao Liu and Shenteng Wan contributed equally to this work. This work was supported by the National Nature Science Foundation of China (22065021), the Key Research Program of Gansu Province

(21YF5GA076), the Province Nature Science Foundation of Gansu (21JR7RA213) and Hongliu Outstanding Youth Teacher Cultivate Project of Lanzhou University of Technology.

References

1. Q. Xie, C. Yi, H. Zhang, H. Xia, G. Xu, C. Miao, L. Yang, T. Shui, W. Zhang, Z. Sun, Stretchable Zn-Ion Hybrid Capacitor with Hydrogel Encapsulated 3D Interdigital Structure, *Advanced Energy Materials*. 2024;14(8):2303592, <https://doi.org/10.1002/aenm.202303592>
2. Y. Wang, S. Sun, X. Wu, H. Liang, W. Zhang, Status and opportunities of zinc ion hybrid capacitors: focus on carbon materials, current collectors, and separators, *Nano-Micro Letters*. 2023;15(1):78, <https://doi.org/10.1007/s40820-023-01065-x>
3. H. Sheng, L. Jiang, Q. Wang, Z. Zhang, Y. Lv, H. Ma, H. Bi, J. Yuan, M. Shao, F. Li, W. Li, E. Xie, Y. Liu, Z. Xie, J. Wang, C. Yu, W. Lan, A soft implantable energy supply system that integrates wireless charging and biodegradable Zn-ion hybrid supercapacitors, *Science Advances*. 2023;9(46):eadh8083, <https://doi.org/10.1126/sciadv.adh8083>
4. J. Yang, J. Ruan, Q. Li, F. Fang, Y. Song, D. Sun, F. Wang, Improved Low-Temperature Performance of Rocking-Chair Sodium-Ion Hybrid Capacitor by Mitigating the De-Solvation Energy and Interphase Resistance, *Advanced Functional Materials*. 2022;32(28):2200566, <https://doi.org/10.1002/adfm.202200566>
5. Y. Liu, L. Wu, Recent advances of cathode materials for zinc-ion hybrid capacitors, *Nano Energy*. 2023;109:108290, <https://doi.org/10.1016/j.nanoen.2023.108290>
6. H. Li, J. Lang, S. Lei, J. Chen, K. Wang, L. Liu, T. Zhang, W. Liu, X. Yan, A high-performance sodium-ion hybrid capacitor constructed by metal–organic framework–derived anode and cathode materials, *Advanced Functional Materials*. 2018;28(30):1800757, <https://doi.org/10.1002/adfm.201800757>
7. H. Li, J. Chen, L. Zhang, K. Wang, X. Zhang, B. Yang, L. Liu, W. Liu, A metal–organic framework-derived pseudocapacitive titanium oxide/carbon core/shell heterostructure for high performance potassium ion hybrid capacitors, *Journal of Materials Chemistry A*. 2020;8(32):16302–11, <https://doi.org/10.1039/d0ta04912c>
8. L. Huang, Z. Gu, W. He, K. Shi, L. Peng, Z. Sheng, F. Zhang, W. Feng, H. Liu, Solvothermal Synthesis and Pyrolysis Toward Heteroatom-Doped Carbon Microspheres for Zinc-Ion Hybrid Capacitors, *Small*. 2024;20(14):2308788, <https://doi.org/10.1002/smll.202308788>
9. Y. Liu, S. Zheng, J. Ma, X. Wang, L. Zhang, P. Das, K. Wang, Z. S. Wu, All 3D printing shape-conformable zinc ion hybrid capacitors with ultrahigh areal capacitance and improved cycle life, *Advanced Energy Materials*. 2022;12(27):2200341, <https://doi.org/10.1002/aenm.202200341>
10. W. Lu, B. B. Xie, C. Yang, C. Tian, L. Yan, J. Ning, S. Li, Y. Zhong, Y. Hu, Phosphorus-Mediated Local Charge Distribution of N-Configuration Adsorption Sites with Enhanced Zincophilicity and Hydrophilicity for High-Energy-Density Zn-Ion Hybrid Supercapacitors, *Small*. 2023;19(45):2302629, <https://doi.org/10.1002/smll.202302629>

11. Y. Zhang, C. Zhu, Y. Xiong, Z. Gao, W. Hu, J. Shi, J. Chen, W. Tian, J. Wu, M. Huang, H. Wang, Multi-Channel Hollow Carbon Nanofibers with Graphene-Like Shell-Structure and Ultrahigh Surface Area for High-Performance Zn-Ion Hybrid Capacitors, *Small Methods*. 2023;7(11):2300714, <https://doi.org/10.1002/smtd.202300714>
12. H. Li, Q. Liao, Y. Liu, Y. Li, X. Niu, D. Zhang, K. Wang, Hierarchically Porous Carbon Rods Derived from Metal-Organic Frameworks for Aqueous Zinc-Ion Hybrid Capacitors, *Small*. 2024;20(15):2307184, <https://doi.org/10.1002/smll.202307184>
13. L. Wei, Y. Chen, Z. Huang, S. Zheng, X. Guo, Redox-enhanced zinc-ion hybrid capacitors with high energy density enabled by high-voltage active aqueous electrolytes based on low salt concentration, *Energy Storage Materials*. 2023;58:30–9, <https://doi.org/10.1016/j.ensm.2023.03.015>
14. X. Gan, C. Zhang, X. Ye, L. Qie, K. Shi, Unveiling the potential of redox electrolyte additives in enhancing interfacial stability for Zn-ion hybrid capacitors, *Energy Storage Materials*. 2024;65:103175, <https://doi.org/10.1016/j.ensm.2023.03.015>
15. H. Li, P. Su, Q. Liao, Y. Liu, Y. Li, X. Niu, X. Liu, K. Olive Leaves-Derived Hierarchical Porous Carbon as Cathode Material for Anti-Self-Discharge Zinc-Ion Hybrid Capacitor, *Small*. 2023;19(49):2304172, <https://doi.org/10.1002/aenm.202001024>
16. T. Huang, B. Gao, S. Zhao, H. Zhang, X. Li, X. Luo, M. Cao, C. Zhang, S. Luo, Y. Yue, Y. Ma, Y. Gao, All-MXenes zinc ion hybrid micro-supercapacitor with wide voltage window based on V2CTx cathode and Ti3C2Tx anode, *Nano Energy*. 2023;111:108383, <https://doi.org/10.1016/j.nanoen.2023.108383>
17. M. S. Javed, T. Najam, I. Hussain, M. Idrees, A. Ahmad, M. Imran, S. S. A. Shah, R. Luque, W. Han, Fundamentals and scientific challenges in structural design of cathode materials for zinc-ion hybrid supercapacitors, *Advanced Energy Materials*. 2023;13(3):2202303, <https://doi.org/10.1002/aenm.202202303>
18. H. Li, J. Wu, L. Wang, Q. Liao, X. Niu, D. Zhang, K. Wang, A zinc ion hybrid capacitor based on sharpened pencil-like hierarchically porous carbon derived from metal–organic framework, *Chemical Engineering Journal*. 2022;428:131071, <https://doi.org/10.1016/j.cej.2021.131071>
19. B. Song, Q. Liu, F. Shi, T. Xue, C. Yang, L. Zang, Porous carbon derived from a by-product of traditional Chinese medicine for high-performance aqueous zinc-ion hybrid supercapacitors, *Diamond and Related Materials*. 2024;142:110785, <https://doi.org/10.1016/j.diamond.2023.110785>
20. H. He, J. Lian, C. Chen, Q. Xiong, C. C. Li, M. Zhang, Enabling multi-chemisorption sites on carbon nanofibers cathodes by an in-situ exfoliation strategy for high-performance Zn–ion hybrid capacitors, *Nano-micro letters*. 2022;14(1):106, <https://doi.org/10.1007/s40820-022-00839-z>
21. Z. Huang, R. Zhang, S. Zhang, P. Li, C. Li, C. Zhi, Recent advances and future perspectives for aqueous zinc-ion capacitors, *Materials Futures*. 2022;1(2):022101, <https://doi.org/10.1021/acsenergylett.8b01426>
22. P. Shang, M. Liu, Y. Mei, Y. Liu, L. Wu, Y. Dong, Z. Zhao, J. Qiu, Urea-mediated monoliths made of nitrogen-enriched mesoporous carbon nanosheets for high-performance aqueous zinc ion hybrid capacitors, *Small*. 2022;18(16):2108057, <https://doi.org/10.1002/smll.202108057>

23. S.-J. Zhang, H. Chen, Y.-X. Xu, C.-S. An, K.-X. Xiang, Facile preparation of Nb₂O₅ microspheres and their excellent electrochemical performance in aqueous zinc-ion hybrid supercapacitors, *Rare Metals*. 2022;41(9):3129–41, <https://doi.org/10.1007/s12598-022-02016-y>
24. W. Zhang, J. Yin, W. Jian, Y. Wu, L. Chen, M. Sun, U. Schwingenschlögl, X. Qiu, H. N. Alshareef, Supermolecule-mediated defect engineering of porous carbons for zinc-ion hybrid capacitors, *Nano Energy*. 2022;103:107827, <https://doi.org/10.1016/j.nanoen.2022.107827>
25. Z. Xu, Z. Sun, J. Shan, S. Jin, J. Cui, Z. Deng, M. H. Seo, X. Wang, O, N-Codoped, Self-Activated, Holey Carbon Sheets for Low-Cost And High-Loading Zinc-Ion Supercapacitors, *Advanced Functional Materials*, 2024;34(14):2302818, <https://doi.org/10.1002/adfm.201807485>
26. X. Fan, P. Liu, B. Ouyang, R. Cai, X. Chen, X. Liu, W. Liu, J. Wang, K. Liu, Polyacrylonitrile Derived Porous Carbon for Zinc-Ion Hybrid Capacitors with High Energy Density, *ChemElectroChem*. 2021;8(18):3572–8, <https://doi.org/10.1002/celec.202100862>
27. Q. Liu, H. Zhang, J. Xie, X. Liu, X. Lu, Recent progress and challenges of carbon materials for Zn-ion hybrid supercapacitors, *Carbon Energy*. 2020;2(4):521–39, <https://doi.org/10.1002/cey2.69>
28. H. Tang, J. Yao, Y. Zhu, Recent developments and future prospects for zinc-ion hybrid capacitors: a review, *Advanced Energy Materials*. 2021;11(14):2003994, <https://doi.org/10.1002/aenm.202003994>
29. J. Lim, N. Cirigliano, J. Wang, B. Dunn, Direct electron transfer in nanostructured sol–gel electrodes containing bilirubin oxidase, *Physical Chemistry Chemical Physics*. 2007;9(15):1809–14, <https://doi.org/10.1039/b618422g>

Figures

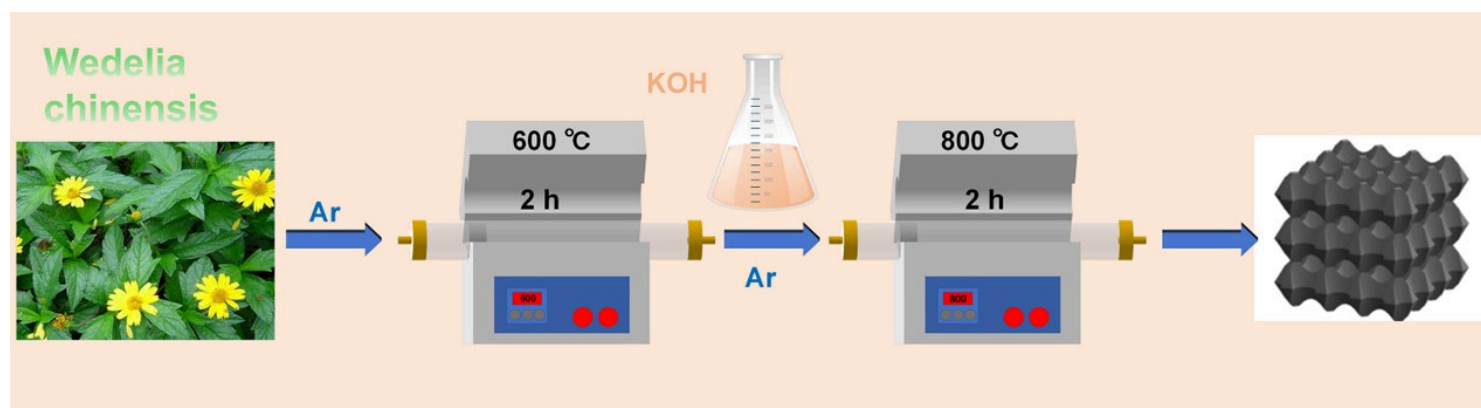


Figure 1

Schematic illustration of material preparation.

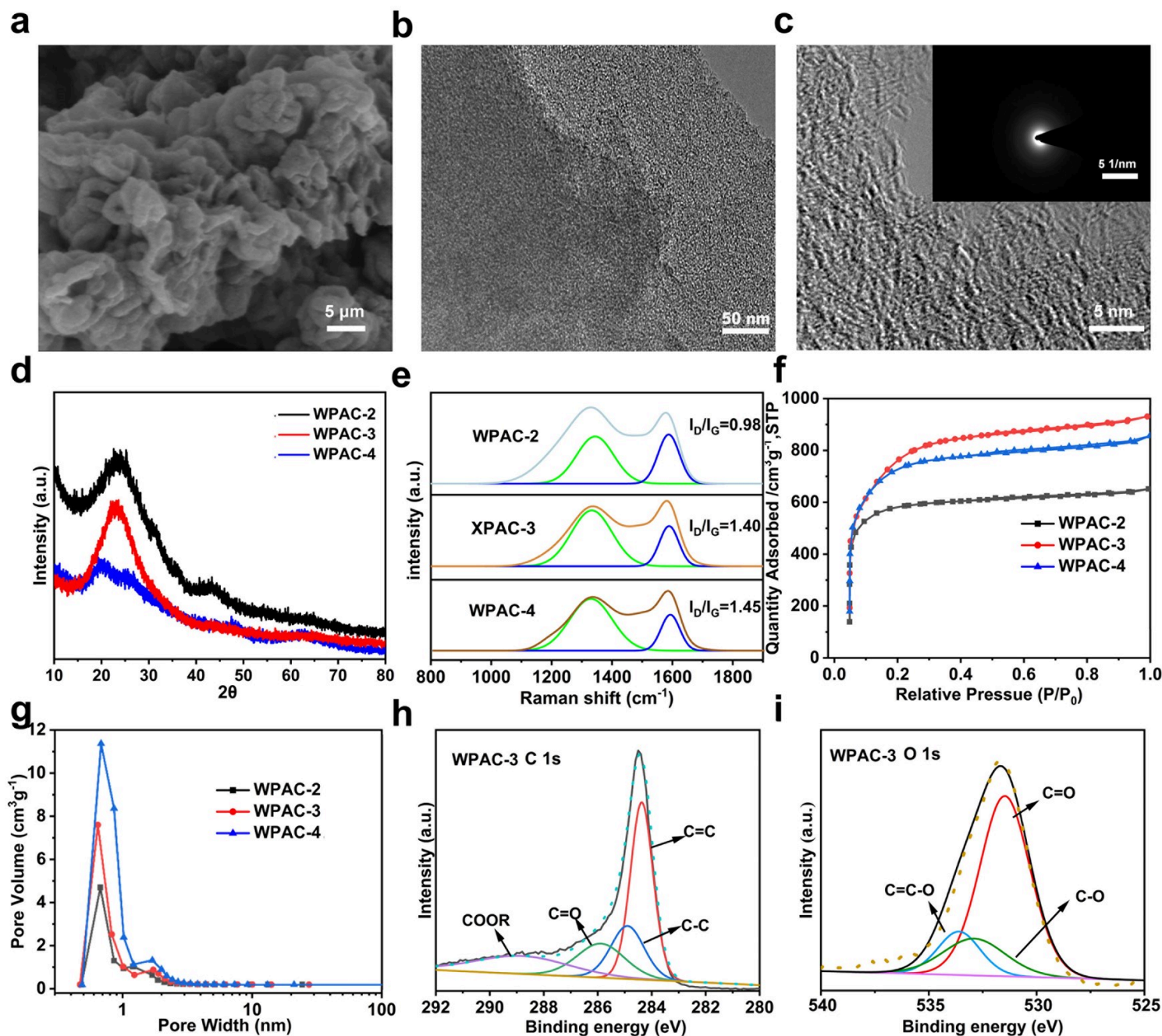


Figure 2

(a) SEM image, (b) TEM image, (c) HRTEM image (inset shows SAED pattern) of WPAC-3. (d) XRD patterns, (e) Raman spectra, (f) N₂ adsorption-desorption isotherms, (g) Pore size distribution plots of WPAC-X samples. The high-resolution XPS spectra of (h) C1s, (i) O1s of WPAC-X.

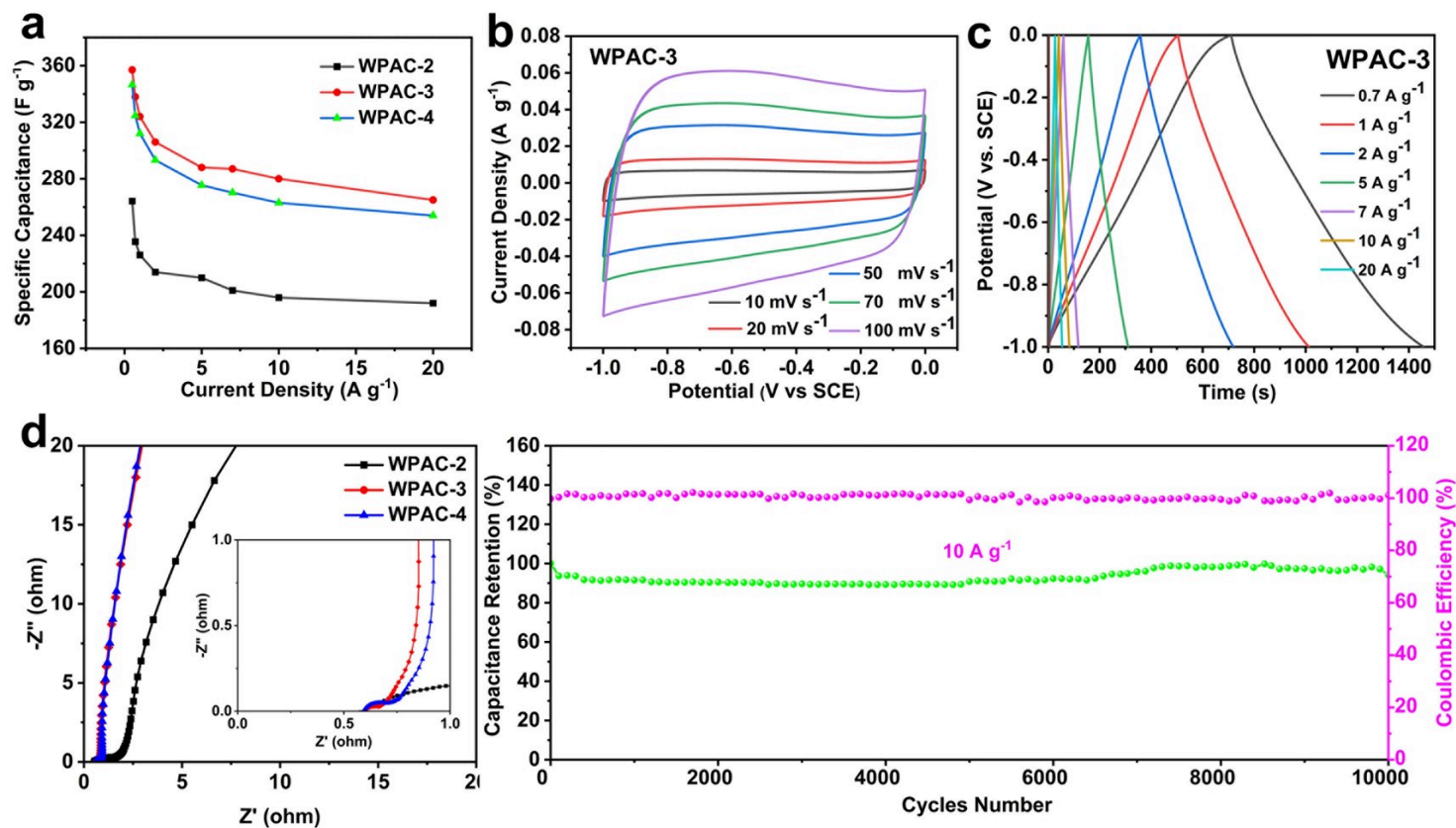


Figure 3

Three-electrode system: (a) Rate capability of WPAC-X at various current densities ranging from 0.7 to 20 A g^{-1} . (b) CV curves, (c) GCD curves of WPAC-3. (d) EIS spectra of WPAC-X materials. (d) Long cycle testing of WPAC-3 at a current density of 10 A g^{-1} .

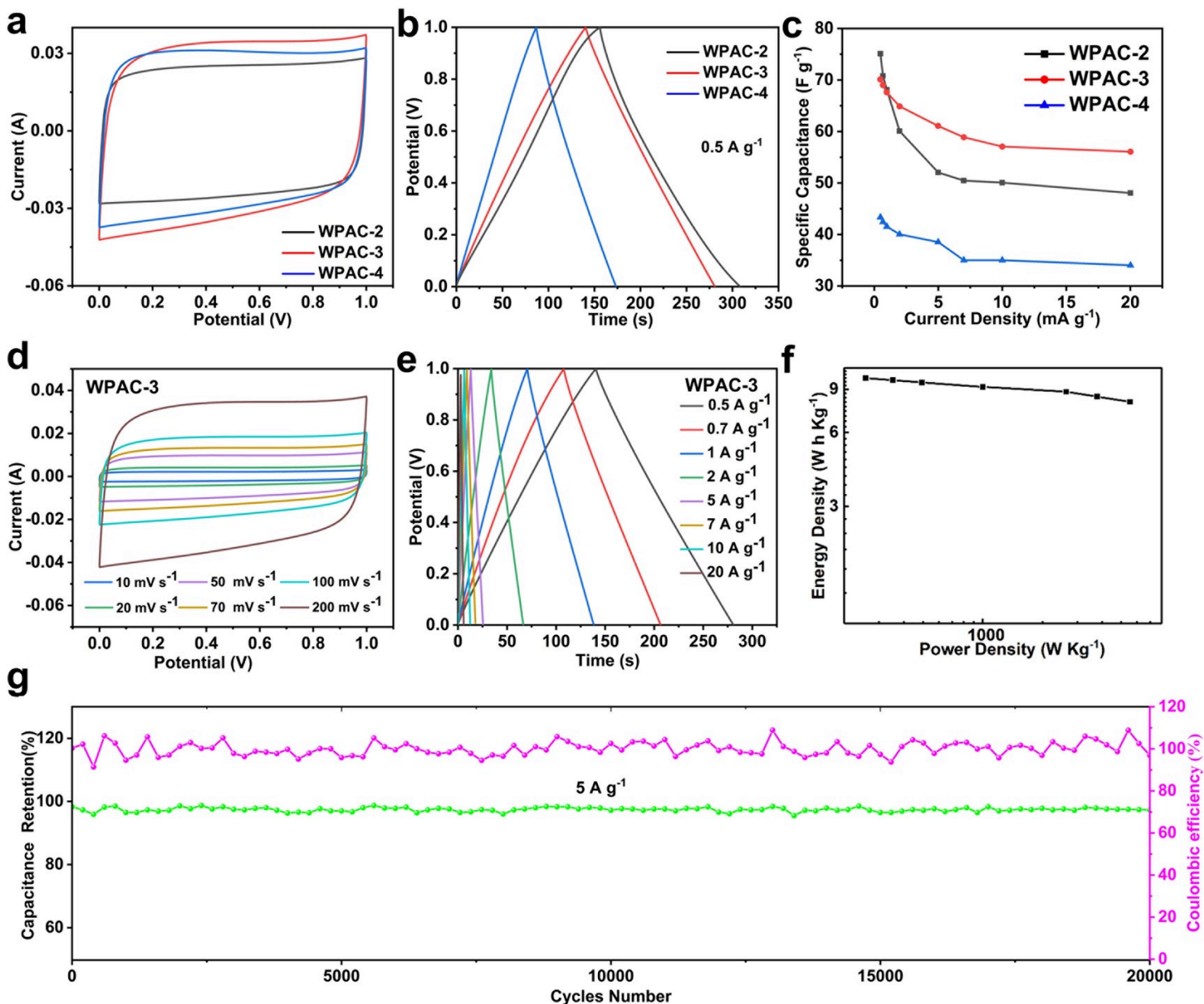


Figure 4

(a) CV curves at 200 mV s^{-1} ; (b) GCD curves at 0.5 A g^{-1} ; (c) Rate capability at various current densities ranging from 0.7 to 20 A g^{-1} , the WPAC-3//WPAC-3 symmetric supercapacitor; (d) CV curves at various sweep speeds; (e) GCD curves of different symmetric supercapacitors; (f) Ragone plot; and (g) Long cycle testing of WPAC-3//WPAC-3 symmetric supercapacitor at a current density of 5 A g^{-1} .

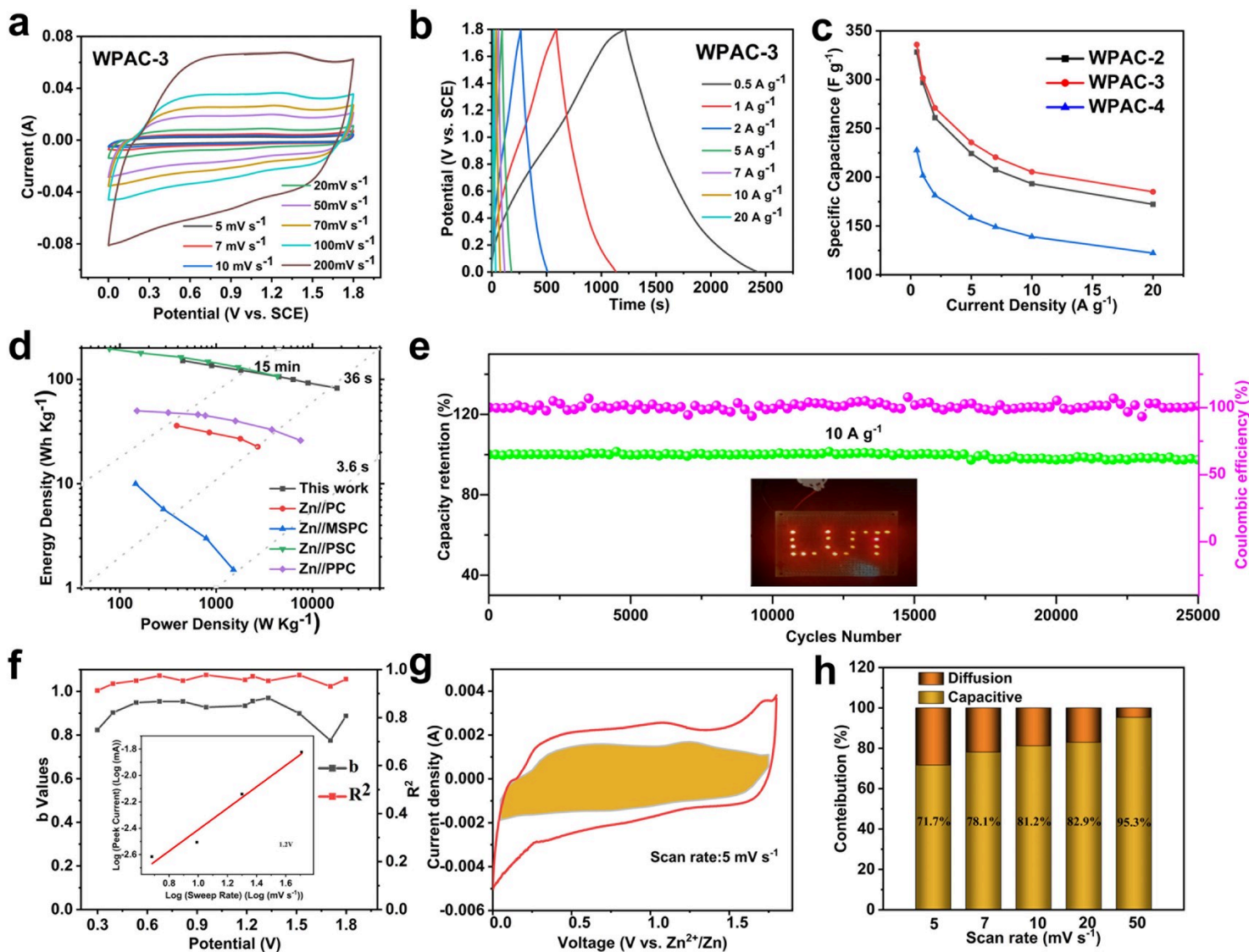


Figure 5

Electrochemical performance of Zn//WPAC-3 ZIHC device: (a) CV curves at different scan rates ranging from 10 to 200 mV s⁻¹; (b) GCD curves at various current densities ranging from 0.5 to 20 A g⁻¹; (c) Rate performance; (d) Ragone plots compared with other ZIHC devices; (e) Cycling performance at 10 A g⁻¹ (inset showed LED array powered by our ZIHC); (f) The corresponding log (peak current) versus log (scan rate) plots at each redox peak; (g) The capacitive-behavior contribution at 5 mV s⁻¹ (the orange region); (h) Capacitive-behavior contribution ratios at a scan rate ranging from 2 to 50 mV s⁻¹.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [SupportingInformationManuscript.docx](#)