Supplementary Information

Composite of Pineapple leaf-derived porous carbon integrated with ZnCo-MOF for high-performance supercapacitor

Xiaoxiao Ma[a], Yunfan Bai[a], Shuangli Chen[a], Zhixian He[b], Pingping Wu[a], Yabing Qi[a] and Sijing Zhang[a*]

[a]School of Chemistry and Chemical Engineering, Xi'an University of Architecture and Technology, Xi'an, 710055, China

[b]Instrumental Analysis Center, Xi'an University of Architecture and Technology, Xi'an, 710055, China

The electrochemical performance of the composites is closely related to the preparation conditions. The preparation conditions of the molar ratio of Zn^{2+} to Co^{2+}, the amount of PLB added, and the carbonization temperature were thus optimized accordingly.

Masses of 1.1891 g, 0.5946 g, 0.2971 g, 0.2971 g, and 0.2971 g (corresponding to 4 mmol, 2 mmol, 1 mmol, 1 mmol, and 1 mmol) of $Zn(NO_3)_2 \cdot 6H_2O$, and masses of 0.2910 g, 0.2910 g, 0.2910 g, 0.5822 g, and 1.1641 g (corresponding to 1 mmol, 1 mmol, 1 mmol, 2 mmol, and 4 mmol) of $Co(NO_3)_2 \cdot 6H_2O$, were separately weighed. These quantities correspond to Zn^{2+} to Co^{2+} molar ratios of 4:1, 2:1, 1:1, 1:2, and 1:4. Additionally, five

*Authors to whom correspondence should be addressed.

Add: 13 Yanta Rd., Xi'an,710055, China; E-mail: sijingzhang@xauat.edu.cn

portions of 0.1000 g of PLB were weighed., and the materials were added to 40 mL of methanol. Following the method described in Section 2.2, a series of composite materials were prepared at a carbonization temperature of 800°C to investigate the effect of the Zn^{2+}/Co^{2+} ratio on the electrochemical performance of the electrode materials.

1 Optimization of the molar ratio of Zn^{2+} to Co^{2+}

The influence of the molar ratio of Zn^{2+} to Co^{2+} on the electrochemical performances (CV, CP, EIS, and specific capacitance) of the electrode are shown in Fig. S1.

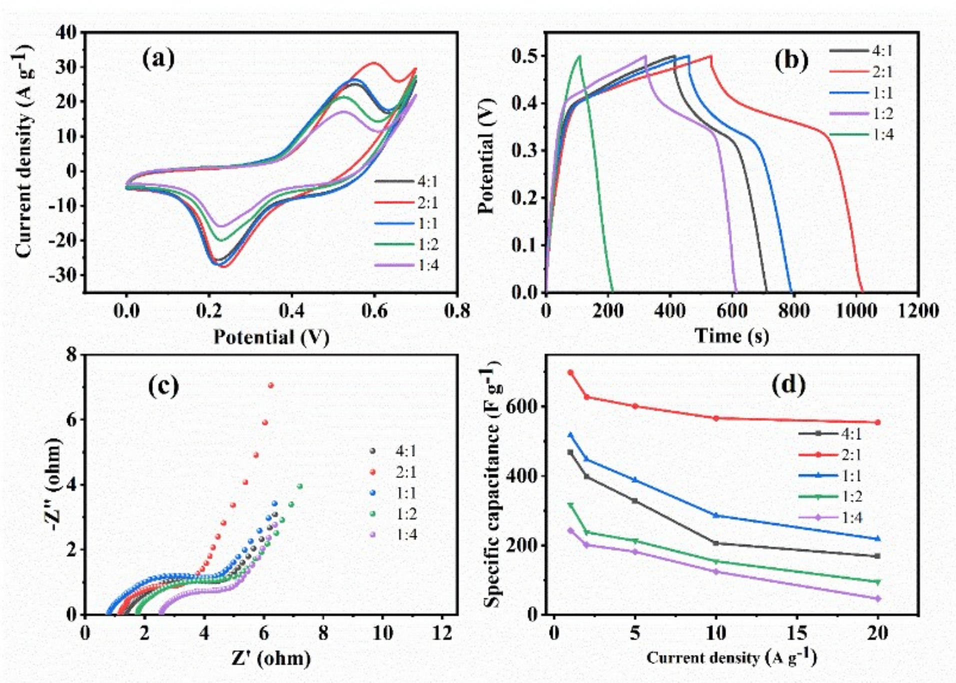

Fig. S1 Electrochemical performance of WBPC with different mass ratios of Zn^{2+} to Co^{2+}: (a)CV curve; (b) GCD curve (c) EIS curve; (d) Specific capacitance diagram

As shown in Fig. S1a, at the same scanning rate (20 mV s^{-1}), redox peaks are clearly observed in the CV curves with different molar ratios, indicating that all five electrodes exhibit Faradaic behavior. As the molar ratio of Zn^{2+} to Co^{2+} gradually increases, the curve area of the electrode first increases and then decreases. It is evident that the CV curve area is largest when the molar ratio of Zn^{2+} to Co^{2+} is 2:1, indicating superior capacitive performance.

This may be due to the optimal molar ratio of Zn^{2+} to Co^{2+} providing active sites, thereby enhancing the chemical reaction behavior. Fig. S1b shows the GCD curves of electrodes with different molar ratios at a current density of 1 A g^{-1}. Under the same current density, the GCD curves exhibit approximately symmetrical behavior. When the molar ratio of Zn^{2+} to Co^{2+} is 2:1, the curve shows the longest discharge time, with clear symmetry and an extended charge-discharge platform, indicating excellent capacitive performance. As shown in Fig. S1c, the EIS spectrum indicates that, in the high-frequency region, the small semicircle radius indicates that electrode material with a Zn^{2+} to Co^{2+} molar ratio of 2:1 exhibits a smaller internal resistance. This suggests that the charge transfer speed of the electrode material is faster and its charge transfer capability is stronger. Additionally, in the low-frequency region, the EIS plot for the electrode material with a 2:1 molar ratio of Zn^{2+} to Co^{2+} shows a steeper slope, indicating lower ion diffusion resistance in the electrolyte and better diffusion effect. According to the GCD curve, the specific capacitance calculations for electrode materials with different molar ratios are shown in Fig. S1d. It is evident that, at a current density of 1-20 A g^{-1}, the electrode material consistently exhibits higher specific capacitance (up to 698.5 F g^{-1}) at a Zn^{2+} to Co^{2+} molar ratio of 2:1 compared to other materials. This suggests that this material undergoes more complete redox reactions, possesses more electroactive sites, and allows for easier electrolyte diffusion, thereby enhancing electrochemical performance.

Based on the above discussion, the electrode material demonstrates the best electrochemical performance when the molar ratio of Zn^{2+} to Co^{2+} is 2:1.

2. Optimization of the PLB addition amount

Similarly, masses of 0.025 g, 0.05 g, 0.10 g, and 0.15 g of PLB were separately weighed. Under the conditions of a Zn^{2+} to Co^{2+} molar ratio of 2:1 and a carbonization temperature of 800 °C, a series of composite materials were prepared to study the influence of PLB addition on the electrochemical performance of the electrodes, as shown in Fig. S2.

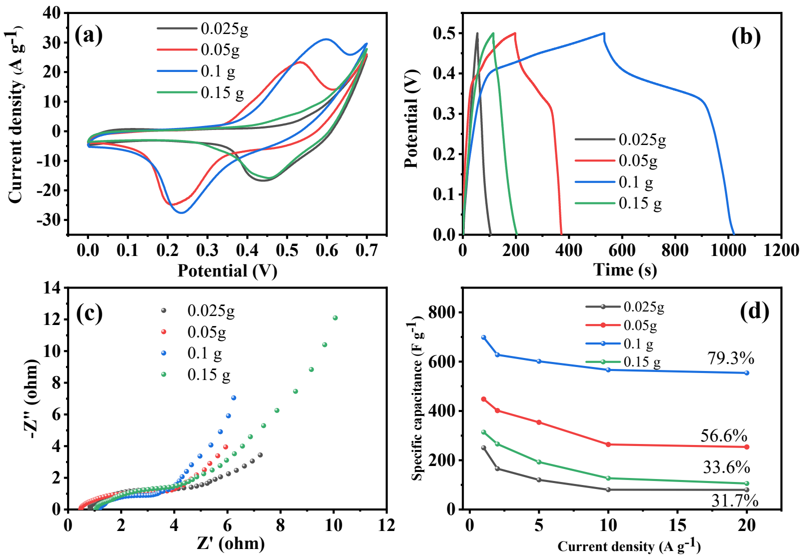

Fig. S2 Electrochemical performance of electrodes with different additions of PLB. (a) CV curve; (b) GCD curve; (c) EIS curve; (d) Specific capacitance

As shown in Fig. S2a, at a scanning rate of 20 mV s^{-1}, the CV curves for different addition amounts show a voltage window of 0-0.7 V for the four electrodes. It can be observed that the closed area of the CV curve is the largest when 0.1 g of PLB is used, and there is a clear oxidation-reduction peak, demonstrating fast Faradaic reaction kinetics and indicating good electrochemical performance. Fig. S2b presents the GCD curves for different amounts of PLB added at a current density of 1 A g^{-1}. The GCD curves exhibit approximately symmetrical behavior under the same current density. When 0.1 g of PLB is added, the GCD curve shows the longest charging and discharging time, with obvious symmetry and extended charge-discharge levels, indicating that an appropriate amount of PLB enhances capacitance performance.

The EIS curve is shown in Fig. S2c. In the high-frequency region, the intercept between the curve and the x-axis represents the internal resistance (Rs) of the material. A smaller x-axis intercept at 0.1 g of PLB indicates the electrode material has lower internal resistance. Additionally, the semicircle radius of the curve in the high-frequency region is associated with charge transfer resistance (Rct). A smaller semicircle radius suggests faster charge transfer and stronger charge transfer capability. Therefore, the electrode material with 0.1 g of PLB has small Rs and Rct. The slope of the straight line in the low-frequency region relates to diffusion resistance (Zw). A larger slope indicates smaller ion diffusion resistance, stronger diffusion ability in the electrolyte, and better diffusion effect. The maximum slope of the curve at 0.1 g PLB demonstrates its large diffusion ability.

The specific capacitance results under different current densities are shown in Fig. S2d. At 1-20 A g^{-1}, the capacitance retention rates for different PLB masses (0.025 g, 0.05 g, 0.10 g, 0.15 g) are 31.7%, 56.6%, 79.3%, and 33.6%, respectively. This indicates that the capacitance retention rate initially increases and then decreases with increasing PLB mass. When 0.10 g of PLB is used, the specific capacitance and capacitance retention rate are optimized. This may be due to the Faradaic reaction of the electrode material being affected at higher current densities, decreasing its capacitance. Excessive PLB results in uneven distribution of ZnCo MOF particles, whereas an appropriate amount of PLB provides a suitable porous structure, enhancing double-layer capacitance and reducing electrolyte ion transport distance.

Based on the above discussion, the electrode material exhibits better electrochemical performance when the PLB addition amount is 0.1 g.

3 Optimization of carbonization temperature

The influence of carbonization temperature on the electrochemical performance of electrodes was investigated under the conditions of a Zn^{2+} to Co^{2+} molar ratio of 2:1 and a PLB addition of 0.1 g, as shown in Fig. S3.

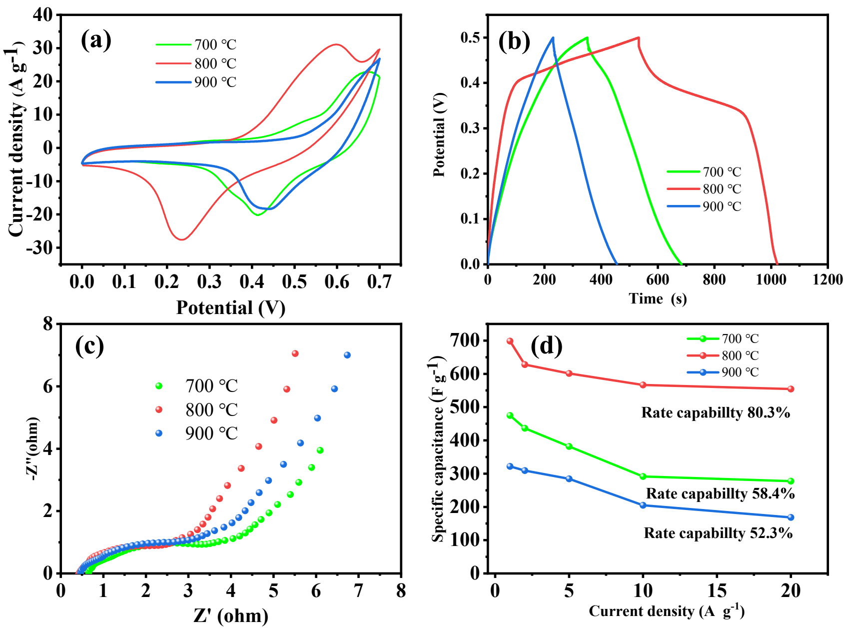

Fig. S3 Electrochemical performance of the composites at different carbonization temperatures. (a) CV curve, (b) GCD curve, (c) EIS curve, (d) Specific capacitance diagram

Fig. S3a shows the CV curves at different carbonization temperatures at a scanning rate of 20 mV s^{-1}. It can be seen that at the same scanning rate, all CV curves exhibit redox peaks, indicating that the electrodes exhibit Faradaic behavior. As the carbonization temperature increases, the curve area first increases and then decreases. The CV curve area is largest at 800 °C, indicating good capacitance performance. This may be due to the volatilization of Zn species at high temperatures providing active sites and enhancing chemical reaction behavior, while excessive temperatures cause the collapse of the carbon framework, reducing the specific surface area and hindering electrochemical reactions.

As shown in Fig. S3b, at a current density of 1 A g^{-1}, the GCD curves of the material exhibit approximately symmetrical behavior at different temperatures. When the carbonization temperature is at 800 °C, the GCD curve shows the longest charging and discharging time, with clear symmetry and a longer charging and discharging plateau, further indicating good capacitive performance, consistent with the CV curve. The EIS spectra are shown in Fig. S3c. In the high-frequency region, the electrode material carbonized at 800 °C has a smaller internal resistance and a smaller semi-circular radius, indicating fast charge transfer speed and strong charge transfer ability.

In the low-frequency region, the EIS curve of the electrode material carbonized at 800°C has a steep slope, indicating lower ion diffusion resistance in the electrolyte and better diffusion effect. This facilitates rapid ion/charge transfer, thereby improving capacitive performance. According to the GCD curve, the specific capacitance of electrode materials at different carbonization temperatures is shown in Fig. S3d. At a current density of 1-20 A g^{-1}, the electrode material carbonized at 800°C consistently exhibits higher specific capacitance and capacitance retention, reaching 80.3%.

To sum up, the optimal conditions to prepare the electrode material are as follows: a Zn^{2+} to Co^{2+} molar ratio of 2:1, a PLB addition of 0.1 g, and a carbonization temperature of 800°C, the material is designated as ZnCo-MOF@PLB-800.