Supporting Information

Balanced Kinetics between Electrodes by Carbon Cloth@ZIF-8 for High Rate Performance Zinc-Ion Hybrid Capacitors

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Experimental Section

Preparation of ZIF-8 derived carbon

ZIF-8 was synthesized *via* dissolved 1.00 g 2-methylimidazole (2-Hmim) in 15 mL of methanol. Then, dissolved 0.42 g $Zn(NO_3)_2 \cdot 6H_2O$ in 5 mL of methanol was added into the above solution for 1 h stirring. After kept undisturbed for 24 h at room temperature, the mixture was washed three times with methanol by centrifugation (10000 rpm, 10 min) and dried in a drying oven at 80 °C for 12 h. The obtained ZIF-8 was heated from room temperature to 915 ºC at a rate of 2 ºC min^{-1}, and kept at 915 ºC for 4 h under continuous Ar gas flow. The obtained black products were further dissolved in 3 M HCl overnight at 80 ºC, then washed by deionized water for several times until pH=7. Finally, the black powders were dried in oven at 120 ºC for 12 h.

Preparation of Carbon cloth@ZIF-8 (CC@ZIF-8)

Carbon cloth (CC) was oxidized by HNO_3 at room temperature for 12 h and then washing by deionized water for several times until pH=7. The oxidized CC was put into the solution of 1.97 mmol 2-Hmim and 59.15 mmol $Zn(CH_3COO)_2 \cdot 2H_2O$ in 64 ml of water and transferred into a Teflon-lined stainless-steel autoclave. The autoclave was sealed and heated to 120 °C and maintained for 8 h, and then allowed to cool down to room temperature. Then CC@ZIF-8 was put into water and ethanol under ultrasonication for several times and then dried in oven at 60 °C for 10 h, which was noted as CC@ZIF-8.

Preparation of Carbon cloth@Zn nanosheets (CC@Zn nanosheets)

CC@Zn nanosheets was synthesized by an electroplating method in three-electrode system. The electroplating was performed at 1.0 V for 300 s in 2 M $ZnSO_4$ electrolyte. After electroplating, the obtained CC@Zn nanosheets was removed from electrolyte, immediately rinsed thoroughly with distilled water and then dried in oven at 60 ºC for 10 h.

Characterization

Field-emission scanning electron micrographs investigations were carried out with a Hitachi FESEM SU8220 instrument. X-ray diffraction (XRD) was carried out on the Rigaku D/Max 2400 diffractometer with Cu Kα radiation (λ=1.5406 Å).

Assembly of aqueous ZICs

Electrodes were made by a mixture of polytetrafluoroethylene (PTFE), acetylene black and ZIF-8 derived carbon (1:1:8). The mixtures were rolled to thin sheets and cut into pieces. Then the carbon sheets were pressed onto carbon cloth and the loading mass of each electrode was ~2 mg cm^{-2}. Four types of ZIC were assembled in 2026 coin-type cells with a bare Zn anode, pure CC/Zn anode CC@ZIF-8/Zn anode or CC@Zn nanosheets/Zn anode (Supporting information, Fig. S4), carbon cathode, 2 M $ZnSO_4$ solution as electrolyte and glass microfiber filter (Whatman) as separator.

Electrochemical Characterization

Electrochemical performance of ZICs were studied by GCD and CV were tested on the electrochemical workstation (Bio-Logic, VP3, France). The potential window for CV and GCD tests was fixed in 0.2–1.8 V. The CV scan rate was in a range of 5 to 500 mV s^{-1}. The GCD curves were measured under the current density ranging from 0.5 to 20 A g^{-1}. The gravimetric capacitance (F g^{-1}) of ZICs was calculated from discharge curves, according to the equation (1):

$$C = \frac{I \times \Delta t}{\Delta V \times m} \tag{1}$$

where Δt, ΔV, I and m are the discharging time (s), voltage window after removing ohmic drop (V), current (mA) and the mass of total carbon cathode (mg), respectively. The energy density was calculated according to the equation (2):

$$E = \frac{1}{2 \times 3.6} C(\Delta V)^2 \tag{2}$$

The power density was calculated according to the equation (3):

$$P = \frac{E \times 3600}{t} \tag{3}$$

where I (A), ∫Vdt (Vs) and V (V) represent the discharge current (A), the integral area under discharge curve and the voltage after ohmic drop, respectively.

Calculation details

The interaction of Zn with CC@ZIF-8 was studied within density functional theory (DFT) calculations using the three-parametrical hybrid functional of Becke[S1] and Lee-Yang-Parr correlation functional[S2] with a pair correction[S3-S4] accounting dispersion interactions (B3LYP-D3 method) as it is implemented in the Jaguar program package (Jaguar, version 10.3, Schrodinger, Inc., New York, NY, 2019). Atomic orbitals of light elements were described by the 6−31G basis set, while the LACVP+ basis set with effective core potential and diffuse functions was used for zinc. The geometry of the models was optimized by an analytical method to the energy change of $2.5 \cdot 10^{-4}$ atomic units for taking into account the shift of atomic position. Geometries of CC@ZIF-8 model were fully optimized. When calculating the CC@ZIF-8 model with zinc the vertical shift of edge graphene atoms was prohibited. For CC@ZIF-8 model, to prevent the movement of two imidazolate rings located perpendicular to the graphene sheet towards adsorbed Zn atoms, we also frozen horizontal positions of their non-coordinated nitrogen atoms. The absence of imaginary frequencies indicated that the obtained structures corresponded to the local minima. For the connection of CC and ZIF-8, we used graphene fragment with two hydroxyl groups located at the basal plane, and the distance between them is close to the diagonal of the square cavity of ZIF-8. Two imidazolate rings were removed from the diagonally located Zn atoms in the model in order to coordinate these atoms to the oxygen atoms of the hydroxyl groups. When optimizing the model, we did not allow graphene to move in the vertical direction relative to the deposited ZIF-8. Compared to isolated ZIF-8 model, the two approaching methyl groups of the imidazolate rings of ZIF-8 grown on CC lead to decrease in the portal size for ZIF-8 cavity.

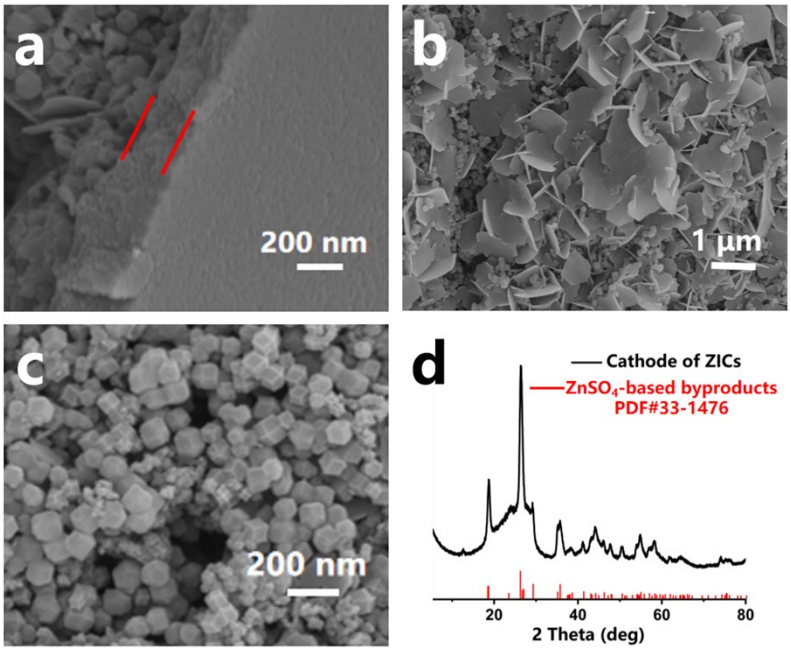

Fig. S1. SEM images of cathodes in different ZICs after 1000 cycles at 50 mV s^{-1}. (a) ZIC, (b) ZIC-CC and (c) ZIC-CC/ZIF-8, respectively. XRD pattern of (d) cathode in ZIC after 1000 cycles at 50 mV s^{-1}.

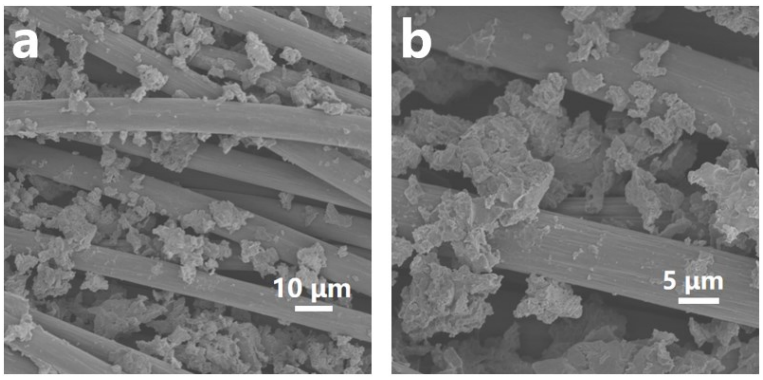

Fig. S2. SEM images of (a-b) large particles of Zn deposits on CC in ZIC-CC after 1000 cycles at 50 mV s^{-1}

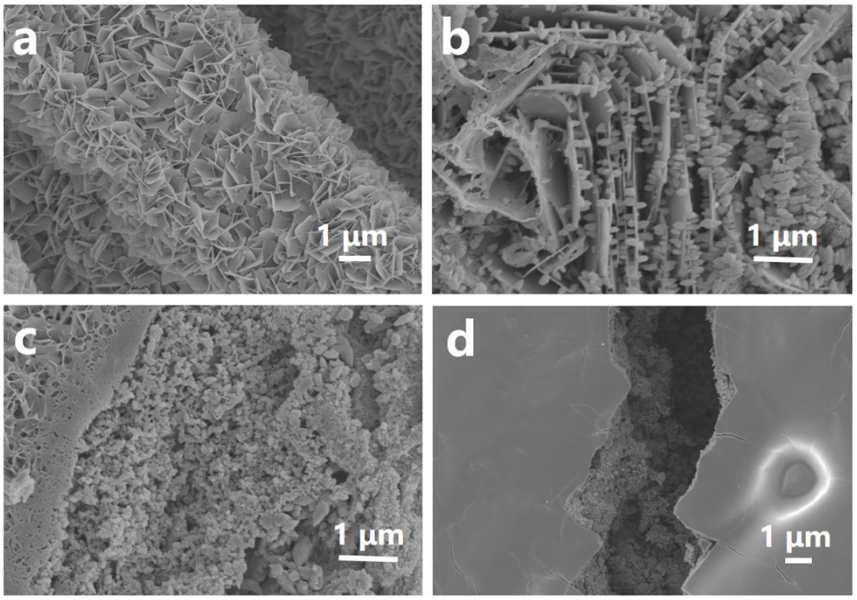

Fig. S3. SEM images of various components in ZIC-CC/Zn nanosheets. (a) Initial CC@Zn nanosheets, (b) CC@Zn nanosheets, (c) Zn metal anode and (d) cathode after 50 cycles at 50 mV s^{-1}.

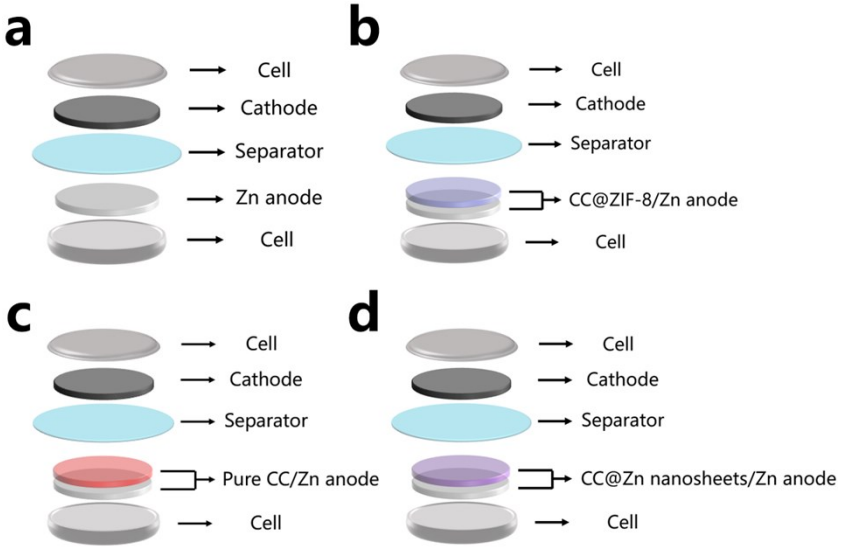

Fig. S4. The structural models of (a) traditional ZICs with one bare Zn anode, (b) modified ZICs with CC@ZIF-8/Zn anode, (c) pure CC/Zn anode and (d) CC@Zn nanosheets/Zn anode.

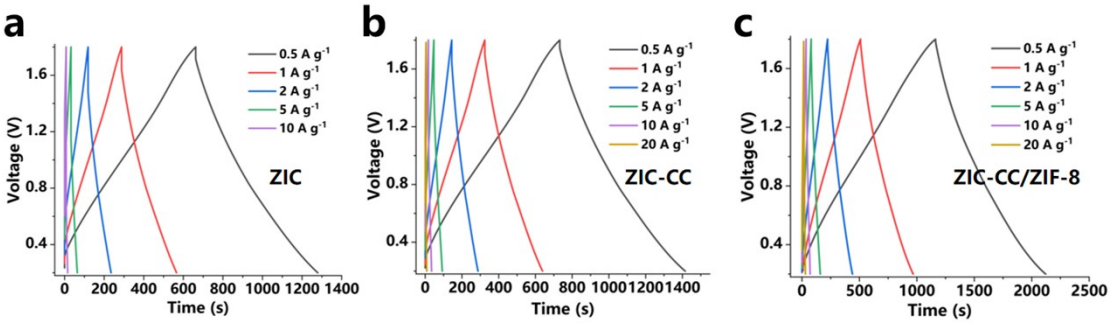

Fig. S5. The GCD curves of (a) ZIC, (b) ZIC-CC and (c) ZIC-CC/ZIF-8.

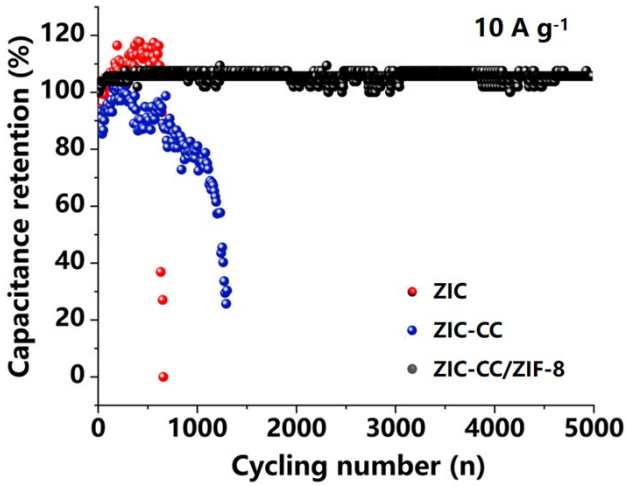

Fig. S6. The cycling performance of ZIC, ZIC-CC and ZIC-CC/ZIF-8 at 10 A g^{-1}.

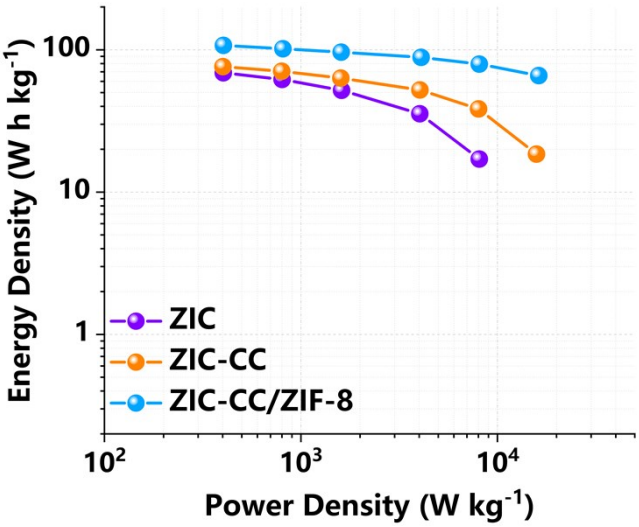

Fig. S7. The Ragone plots of ZIC, ZIC-CC and ZIC-CC/ZIF-8.

Table S1. Comparison of ZIC-CC/ZIF-8 with other advanced ZICs.

ZICs	Electrolyte	V (V)	C	Ref.
ZIC-CC/ZIF-8	**2 M $ZnSO_4$**	**0.2-1.8**	**302 F g^{-1} at 0.5 A g^{-1}** **188 F g^{-1} at 20 A g^{-1}**	**This work**
LDC based ZIC	1 M $ZnSO_4$	0.2-1.8	127.7 mAh g^{-1} at 0.5 A g^{-1} 42.8 mAh g^{-1} at 20 A g^{-1}	Ref. S5
PSC-A600 based ZIC	1 M $Zn(CF_3SO_3)_2$	0.2-1.8	413.3 F g^{-1} at 0.2 A g^{-1} 184.1 F g^{-1} at 20 A g^{-1}	Ref. S6
PC-800 based ZIC	3 M $Zn(ClO_4)_2$	0-1.9	179.8 mAh g^{-1} at 0.1 A g^{-1} 78.4 mAh g^{-1} at 20 A g^{-1}	Ref. S7
TiN based ZIC	2 M $ZnSO_4$	0.1-1.9	489.8 F g^{-1} at 0.2 A g^{-1} 171.1 F g^{-1} at 6.4 A g^{-1}	Ref. S8
AC based ZIC	2 M $ZnCl_2$	0.2-1.8	229.4 F g^{-1} at 1 A g^{-1} 120 F g^{-1} at 20 A g^{-1}	Ref. S9
GH films based ZIC	2 M $ZnSO_4$	0.2-1.8	99.3 mAh g^{-1} at 0.1 A g^{-1} 60 mAh g^{-1} at 20 A g^{-1}	Ref. S10
MXene-rGO based ZIC	2 M $ZnSO_4$	0.2-1.6	128.6 F g^{-1} at 0.4 A g^{-1} 40.3 F g^{-1} at 6 A g^{-1}	Ref. S11

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