

Supporting Information

for

N, O Co-doped Hierarchically Carbon Cathode for High-performance Zn-Ion Hybrid Supercapacitor with Enhanced Pseudocapacitance

Xiaoyang Deng^a, Jiajun Li^a, Shan Zhu^a, Junwei Sha^a, Liying Ma^{a}, and Naiqin Zhao^{abc*}*

^a School of Materials Science and Engineering and Tianjin Key Laboratory of Composites and Functional Materials, Tianjin University, Tianjin 300350, China
E-mail: lyma@tju.edu.cn, nqzhao@tju.edu.cn

^b Collaborative Innovation Center of Chemical Science and Engineering, Tianjin 300350, China

^c Key Laboratory of Advanced Ceramics and Machining Technology, Ministry of Education, Tianjin, 300350, China

Calculation

(1) For the Trasatti and Dunn analysis[1-3]

In order to resolve quantitatively the contribution from capacitive and diffusion-controlled processes in the total charge, the dependency of the voltammetric sweep rate on the current response was studies. The total measured voltammetric charge could be expressed as a function of scan rate through the following equations:

$$i(V) = k_1v + k_2v^{1/2} \quad (\text{S1})$$

$$i(V)/v^{1/2} = k_1v^{1/2} + k_2 \quad (\text{S2})$$

where, $i(V)$ is the measured current as a function of potential that is considered to be comprised of both capacitive currents (which vary as k_1v) and diffusion-controlled currents (which vary as $k_2v^{1/2}$). By determining constants k_1 and k_2 , the fraction of the current from diffusion and capacitance can be distinguished.

(2) The specific capacity (C, mAh g-1) for ZHSs was calculated from the galvanometric charge-discharge curves using the following equations:

$$C = 2I\int V dt/3.6Vm \quad (\text{S3})$$

where I (A), $\int V dt$ (Vs), V (V) and m (g) represent the discharge current (A), the integral area under charge/discharge curve, the voltage after ohmic drop, and the mass of active material in cathode, respectively.

Energy density and power density for the ZHS device were calculated based on the mass of active material of cathode using the following equations:

$$E = I\int V dt/3.6m \quad (\text{S4})$$

$$P = 3600E/t \quad (\text{S5})$$

Where E (Wh kg^{-1}) is the energy density, P (W kg^{-1}) is the power density, t (s) is the discharge time.

Supporting Figure

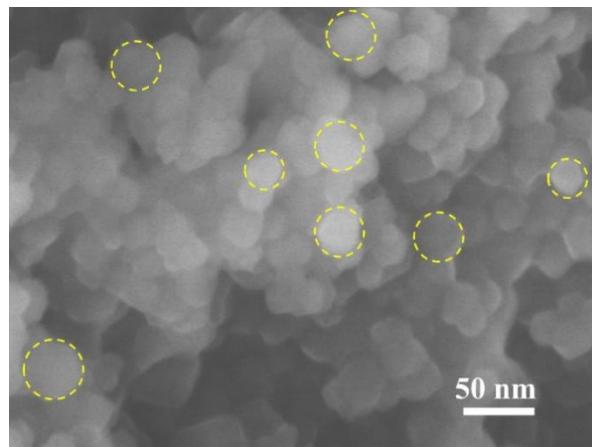


Fig. S1. SEM image of ZIF-8.

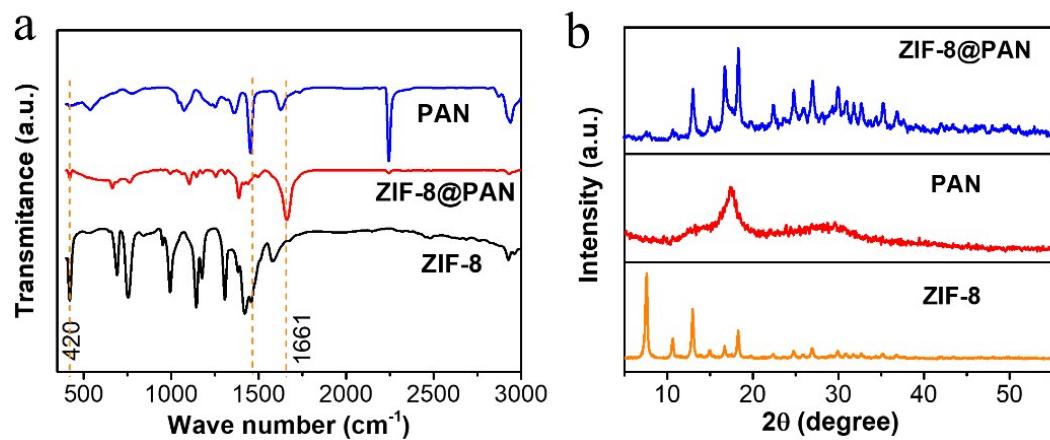


Fig. S2. FTIR spectra (a) and XRD patterns (b) of ZIF-8 and ZIF-8@PAN.

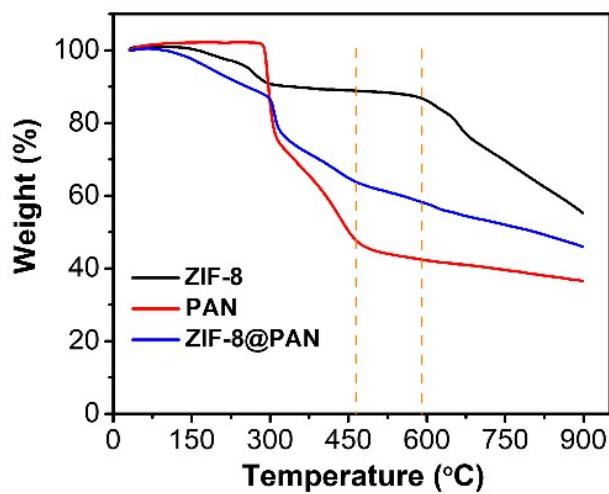


Fig. S3. TG curves of ZIF-8, PAN and ZIF-8@PAN

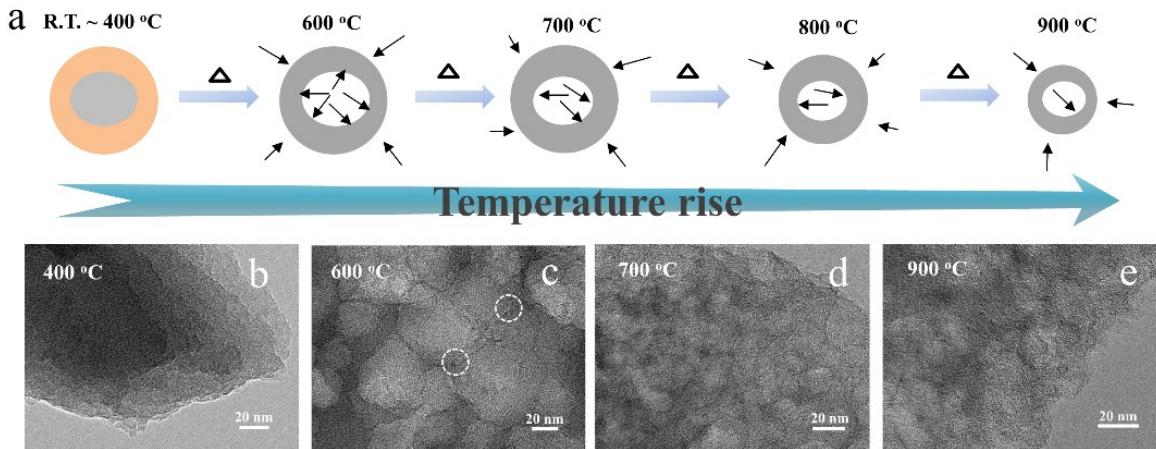


Fig. S4. (a) the formation process of HPC and (b-e) the TEM images of samples obtained at different temperature (holding on 2 h).

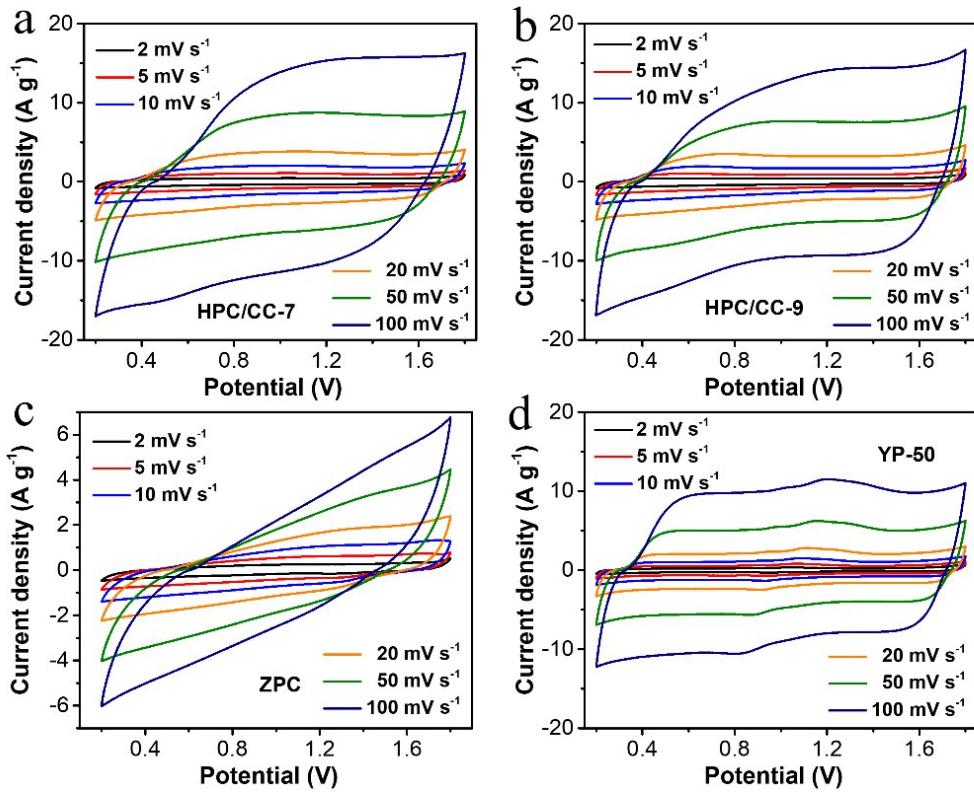


Fig. S5. CV curves of ZHSs at different scan rates.

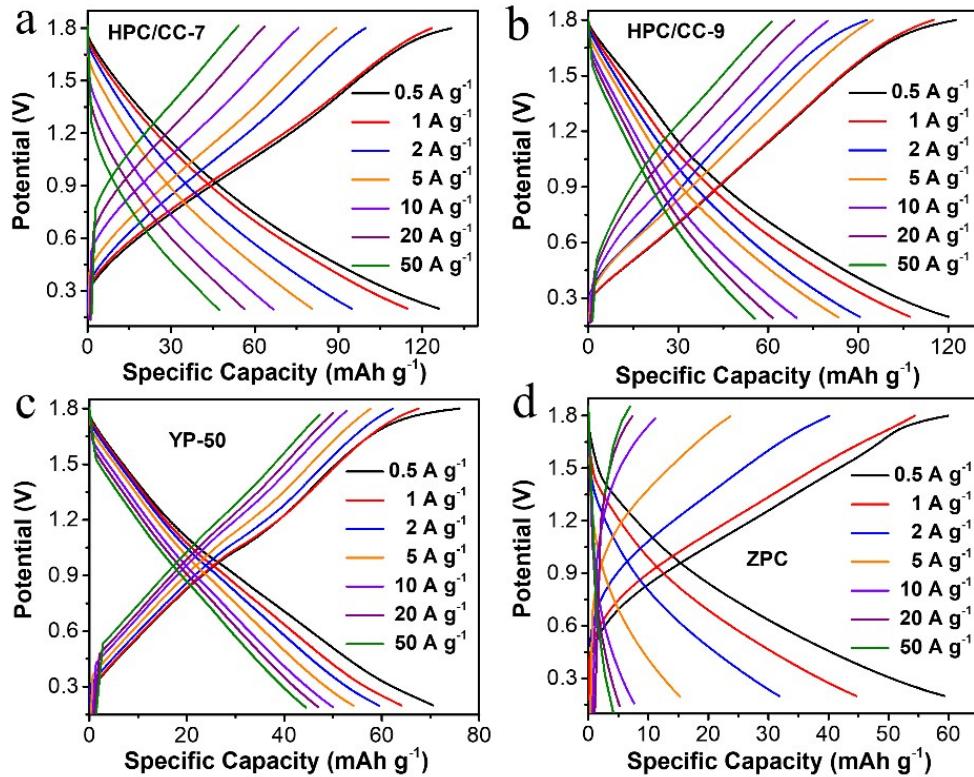


Fig. S6. GCD curves of the ZHSs at different density currents.

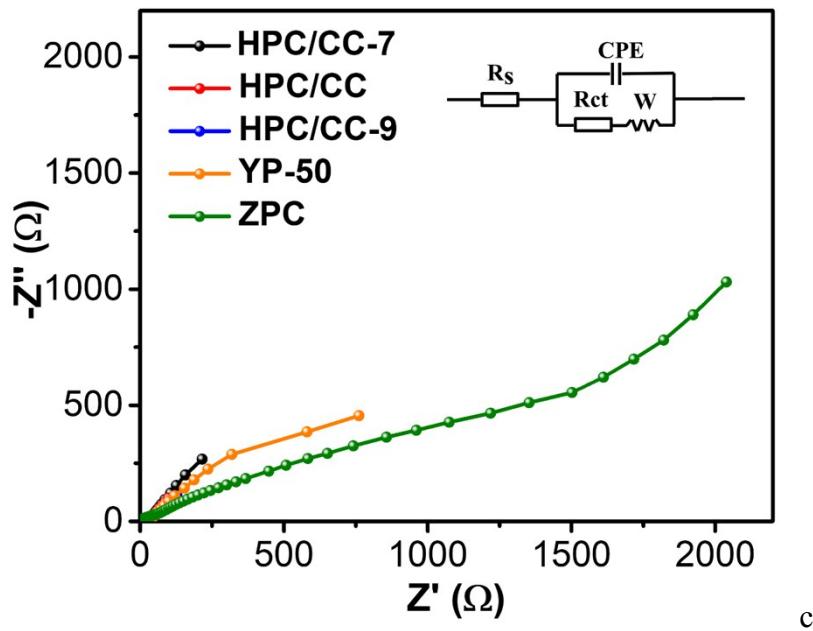


Fig. S7. EIS spectra of ZHSs (inset: the electrical equivalent circuit used for fitting EIS spectra).

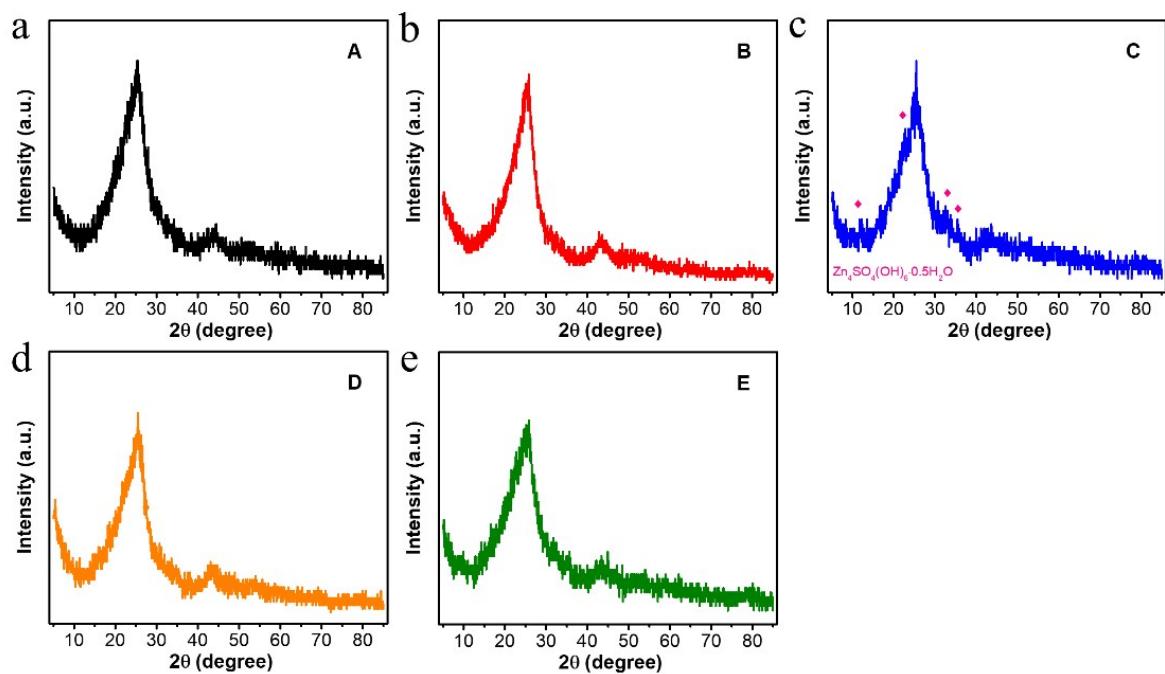


Fig. S8. XRD patterns of HPC/CC electrodes at different discharge-charge stages.

Supporting Tables

Table S1. The texture characteristics of all samples.

Sample	S _{BET} ^a (m ² g ⁻¹)	V _{total} ^b (cm ³ g ⁻¹)	V _{micro} ^c (cm ³ g ⁻¹)	V _{meso} ^d (cm ³ g ⁻¹)	S _{micro} ^c (m ² g ⁻¹)	S _{meso} ^d (m ² g ⁻¹)
HPC/CC-7	276.49	0.161	0.095	0.066	232.06	44.43
HPC/CC	197.45	0.139	0.063	0.076	149.86	47.59
HPC/CC-9	168.10	0.099	0.056	0.043	135.95	32.15

^a The specific surface area were calculated by using multiple BET method.

^b The total pore volume were calculated at the relative pressure of 0.99.

^c The pore volume and specific surface area of micropores were calculated by using t-plot method.

^d The pore volume of mesopores and specific surface area were calculated by subtracting the volume of micropores from the total volume.

Table S2. XPS results of all samples.

Sample	C 1s (at. %)	N 1s (at. %)	O 1s (at. %)
HPC/CC-7	84.35	10.25	5.40
HPC/CC	89.73	6.52	3.76
HPC/CC-9	95.07	2.38	2.54

Table S3. Performance comparison of aqueous ZHSs based on different cathodes.

Materials	Electrolyte	Self-standing	Current Density (A g ⁻¹)	Capacity (mAh g ⁻¹)	Reference
HPC/CC	2M ZnSO ₄	Yes	0.5	138.5	This work
			20	75	
AC	2M ZnSO ₄	No	0.1	121	[4]
			20	41	
AC	1M Zn(CF ₃ SO ₃) ₂	No	0.1	144 (F g ⁻¹)	[5]
			2	64 (F g ⁻¹)	
AC	0.5M ZnSO ₄	No	0.1	100	[6]
			4	69.2	
aMEGO	3M Zn(CF ₃ SO ₃) ₂	No	0.1	210 (F g ⁻¹)	[7]
			20	110 (F g ⁻¹)	
LDC	1M ZnSO ₄	No	0.5	127.7	[8]
			20	42.8	
FAC	2M ZnSO ₄	No	0.1	435 (F g ⁻¹)	[9]
			20	198 (F g ⁻¹)	
DV2C@CNT	1M ZnSO ₄	Yes	0.5	190.2 (F g ⁻¹)	[10]
			10	90.2 (F g ⁻¹)	
RuO ₂ ·H ₂ O	Zn(CF ₃ SO ₃) ₂	No	0.1	122	[11]
			20	98	
Ti3C2	2M ZnSO ₄	Yes	0.5	132	[12]
			3	121	
MCHSs	2M ZnSO ₄	No	0.1	174.7	[13]
			10	96.9	
AC	2M ZnSO ₄	No	0.5	468 (F g ⁻¹)	[14]
			20	150 (F g ⁻¹)	
HCSs	ZnSO ₄ PAM	No	0.5	86.8	[15]
			4	47.1	

Reference

- [1] S. Ardizzone, G. Fregonara, S. Trasatti, “Inner” and “outer” active surface of RuO₂ electrodes, *Electrochim. Acta* 35 (1990) 263-267. [http://dx.doi.org/10.1016/0013-4686\(90\)85068-x](http://dx.doi.org/10.1016/0013-4686(90)85068-x)
- [2] J. Come, P.L. Taberna, S. Hamelet, C. Masquelier, P. Simon, Electrochemical Kinetic Study of LiFePO₄ Using Cavity Microelectrode, *J. Electrochem. Soc.* 158 (2011) A1090-A1093. <http://dx.doi.org/10.1149/1.3619791>
- [3] J. Wang, J. Polleux, J. Lim, B. Dunn, Pseudocapacitive Contributions to Electrochemical Energy Storage in TiO₂(Anatase) Nanoparticles, *J. Phy. Chem. C* 111 (2007) 14925-14931. <http://dx.doi.org/10.1021/jp074464w>
- [4] L. Dong, X. Ma, Y. Li, L. Zhao, W. Liu, J. Cheng, C. Xu, B. Li, Q.-H. Yang, F. Kang, Extremely safe, high-rate and ultralong-life zinc-ion hybrid supercapacitors, *Energy Storage Mater.* 13 (2018) 96-102. <http://dx.doi.org/10.1016/j.ensm.2018.01.003>
- [5] H. Wang, M. Wang, Y. Tang, A novel zinc-ion hybrid supercapacitor for long-life and low-cost energy storage applications, *Energy Storage Mater.* 13 (2018) 1-7. <http://dx.doi.org/10.1016/j.ensm.2017.12.022>
- [6] A. Xia, X. Pu, Y. Tao, H. Liu, Y. Wang, Graphene oxide spontaneous reduction and self-assembly on the zinc metal surface enabling a dendrite-free anode for long-life zinc rechargeable aqueous batteries, *Appl. Surf. Sci.* 481 (2019) 852-859. <http://dx.doi.org/10.1016/j.apsusc.2019.03.197>
- [7] L. Wang, S.S. Welborn, H. Kumar, M. Li, Z. Wang, V.B. Shenoy, E. Detsi, High-Rate and Long Cycle-Life Alloy-Type Magnesium-Ion Battery Anode Enabled Through (De)magnesiation-Induced Near-Room-Temperature Solid–Liquid Phase Transformation, *Adv. Energy Mater.* 9 (2019) 1902086.

<http://dx.doi.org/10.1002/aenm.201902086>

- [8] Y. Lu, Z. Li, Z. Bai, H. Mi, C. Ji, H. Pang, C. Yu, J. Qiu, High energy-power Zn-ion hybrid supercapacitors enabled by layered B/N co-doped carbon cathode, *Nano Energy* 66 (2019) 104132. <http://dx.doi.org/10.1016/j.nanoen.2019.104132>
- [9] C. Liu, J.C. Wu, H. Zhou, M. Liu, D. Zhang, S. Li, H. Gao, J. Yang, Great Enhancement of Carbon Energy Storage through Narrow Pores and Hydrogen-Containing Functional Groups for Aqueous Zn-Ion Hybrid Supercapacitor, *Molecules* 24 (2019) 2589. <http://dx.doi.org/10.3390/molecules24142589>
- [10] C. Wang, S. Wei, S. Chen, D. Cao, L. Song, Delaminating Vanadium Carbides for Zinc-Ion Storage: Hydrate Precipitation and H^+/Zn^{2+} Co-Action Mechanism, *Small Methods* 3 (2019) 1900495. <http://dx.doi.org/10.1002/smtd.201900495>
- [11] L. Dong, W. Yang, W. Yang, C. Wang, Y. Li, C. Xu, S. Wan, F. He, F. Kang, G. Wang, High-Power and Ultralong-Life Aqueous Zinc-Ion Hybrid Capacitors Based on Pseudocapacitive Charge Storage, *Nano-Micro Letters* 11 (2019) 94. <http://dx.doi.org/10.1007/s40820-019-0328-3>
- [12] Q. Yang, Z. Huang, X. Li, Z. Liu, H. Li, G. Liang, D. Wang, Q. Huang, S. Zhang, S. Chen, C. Zhi, A Wholly Degradable, Rechargeable Zn-Ti₃C₂ MXene Capacitor with Superior Anti-Self-Discharge Function, *ACS Nano* 13 (2019) 8275-8283. <http://dx.doi.org/10.1021/acsnano.9b03650>
- [13] P. Liu, W. Liu, Y. Huang, P. Li, J. Yan, K. Liu, Mesoporous hollow carbon spheres boosted, integrated high performance aqueous Zn-Ion energy storage, *Energy Storage Mater.* 25 (2020) 858-865. <http://dx.doi.org/10.1016/j.ensm.2019.09.004>
- [14] G.H. An, J. Hong, S. Pak, Y. Cho, S. Lee, B. Hou, S. Cha, 2D Metal Zn Nanostructure Electrodes for High-Performance Zn Ion Supercapacitors, *Adv. Energy Mater.* 10 (2019) 1902981. <http://dx.doi.org/10.1002/aenm.201902981>

[15] S. Chen, L. Ma, K. Zhang, M. Kamruzzaman, C. Zhi, J.A. Zapien, A flexible solid-state zinc ion hybrid supercapacitor based on co-polymer derived hollow carbon spheres, *J. Mater. Chem. A* 7 (2019) 7784-7790.

<http://dx.doi.org/10.1039/C9TA00733D>