

Supporting Information

Zn₂SiO₄@C Submicro-Ellipsoid Assembled from Oriented Nanorods with Outstanding Rate Performance for Li-Ion Capacitors

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Experimental Section

Synthesis of Zn₂SiO₄@C submicro-ellipsoid hybrids: The all reagents used to prepare Zn₂SiO₄@C hybrids are analytical grade. SiO₂ nanoparticles are prepared by Stöber method. Briefly, ammonia (5 mL) and tetraethyl orthosilicate (TEOs, 3 mL) were added into 350 mL ethanol and water mixed solvent (ethanol: water = 4 : 1, V/V), and stirred at 25 °C for 4 h. The SiO₂ powder can be obtained after centrifugation, and then dried at 50 °C in a blast drying oven for 12 h.

SiO₂ (1 mmol) and NaOH (1 mmol) were added into 20 mL deionized water and

disperse under ultrasound (400 kW, 0.5 h). Then, $\text{Zn}(\text{CH}_3\text{COO})_2$ solution (10 mL, 0.2 M) was added into the above solution drop by drop and stirred at 25 °C. After stirring for 30 min, the mixed solution was added into the Teflon, and reacted at 200 °C for 3 h. After the reaction, the mixture was centrifuged and washed with deionized water for several times. After drying at 50 °C for 12 h, Zn_2SiO_4 precursor was obtained and named as ZSO-3. With the similar steps and extending the reaction time to 5 h and 8 h, the Zn_2SiO_4 precursors were obtained and named as ZSO-5 and ZSO-8, respectively.

1 mmol of ZSO-5 precursor was firstly stirring in poly dimethyl diallyl ammonium chloride (PDDA) aqueous solution (400 mL, 10 μM) at 25 °C. After 30 min, the PDDA modified precursor can be obtained by centrifugation and washed with deionized water for three times. The obtained PDDA modified ZSO-5 precursor was then added to poly(sodium-*p*-styrenesulfonate) (PSS) aqueous solution (250 mL, 10 μM). After stirring at 25 °C for 30 min, PDDA/PSS co-modified ZSO-2 precursor was obtained by centrifugation.

1 mol of PDDA/PSS co-modified ZSO-5 precursor was dispersed in 25 mL methanol via ultrasound and the dispersion was added into the methanol solutions of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.06 M, 25 mL) and 2-methylimidazole (0.48 M, 25 mL). After stirring at 0 °C for 1 h and at 25 °C for 3 h, the powders were obtained through centrifugation, washed with methanol for three times, and dried at 50 °C for one night. The product was subsequently treated under Ar atmosphere at 150 °C for 1 h and at 800 °C for 2 h with a heating rate of 5 °C min^{-1} . The hybrid obtained after heating was named as ZSC-1. Increasing the concentration of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution to 0.07 M

and 0.08 M (the mole ratio of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 2-methylimidazole is 1:8), the products can be obtained and named as ZSC-2 and ZSC-3 respectively.

Synthesis of graphene hydrogel cathode: The graphene oxide (GO) were synthesized by modified Hummers' method as our previous work. ^[1] Briefly, 100 mL of GO dispersion (2 mg mL^{-1}) was poured into a 150 mL Teflon autoclave which was placed in a $180 \text{ }^\circ\text{C}$ oven. After 12 h, graphene hydrogel can be obtained through freeze-dried.

Electrochemical measurements: The active materials, conductive agent (Ketjenblack carbon) and binder (LA133, a water dispersion of acrylonitrile polycopolymer) (8:1:1 w/w/w) were mixed uniformly with deionized water and the mixture was coated onto a copper foil. After drying at $100 \text{ }^\circ\text{C}$ for 12 h, the loaded Cu foil was cut into disk with a diameter of 12 mm. The mass loading of the active material on each disk electrodes was 1 mg approximately. The separator is Celgard 2500 membrane and counter electrode is lithium metal, respectively. A solution of 1.0 M LiPF_6 in mixed dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), and ethylene carbonate (EC) at a volume ratio of 1:1:1 was used as the electrolyte. Prior to full LIC cell assembly, the ZSC-2 electrode was pre-lithiated by a simple surface treatment, specifically by placing the electrolyte-wetted ZSC-2 electrodes in direct contact with the Li metal for more than 1 h.

LAND CT2001A battery test system was used to test the galvanostatic charge-discharge measurements from 0.01 to 3.0 V (vs. Li/Li^+) and CHI660E electrochemical workstation was used to carry out the cyclic voltammetry (CV) measurements. The coin

cell was set still for at least 12 h before the test.

The energy density (E) and power densities (P) were calculated using the following Equation (1–3). In the equations, t is the discharge time (t_1 and t_2 are the initial and final discharge time, respectively), I ($A\ g^{-1}$) is the discharge current density, and V (V) is the average discharge voltage (~ 2.005 V).

$$E = \int_{t_1}^{t_2} IV dt \quad (1)$$

$$P = E/t \quad (2)$$

$$V = \frac{(V_{max} + V_{min})}{2} \quad (3)$$

Materials characterization: Scanning electron microscope (FEI Nova Nano 450) was used at an accelerating voltage of 10 kV to examine the morphologies of the hybrids. TEM measurements was prepared by dropping the dispersion liquid of the samples onto the copper grid. X-ray photoelectron spectroscopy (XPS) was obtained with the spectrometer (ESCALAB 250Xi). X-ray diffraction (XRD, Bruker D8 Focus, $1.5418\ \text{\AA}$) was used by using the Cu Ka radiation to analyze the ingredient of samples. The thermogravimetric analyzer (TGA, SDT2960) was employed to analysis the carbon content of the samples. Raman spectrometer (LabRAM HR Evolution) was used to test with a 532 nm laser excitation. The Brunauer-Emmett-Teller (Micromeritics, ASAP2020M) equation was used to calculate the specific surface area based on the N_2 adsorption-desorption isotherms with the Builder SSA-4200 instrument.

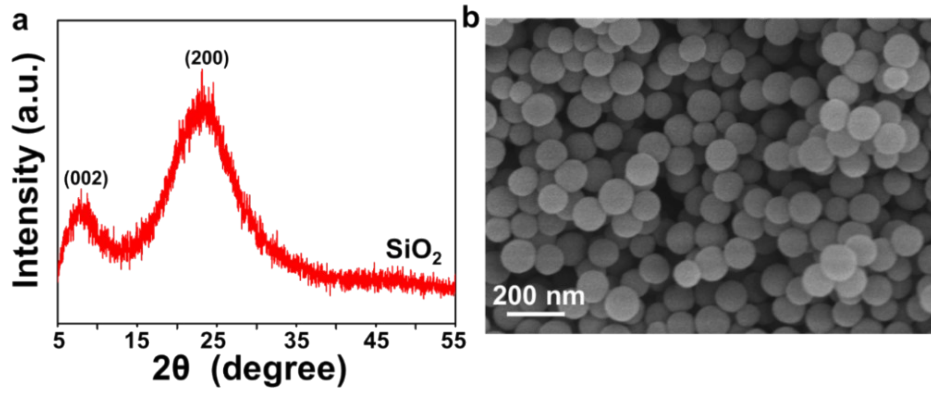


Fig. S1 a) XRD pattern of SiO_2 and b) SEM image of SiO_2 .

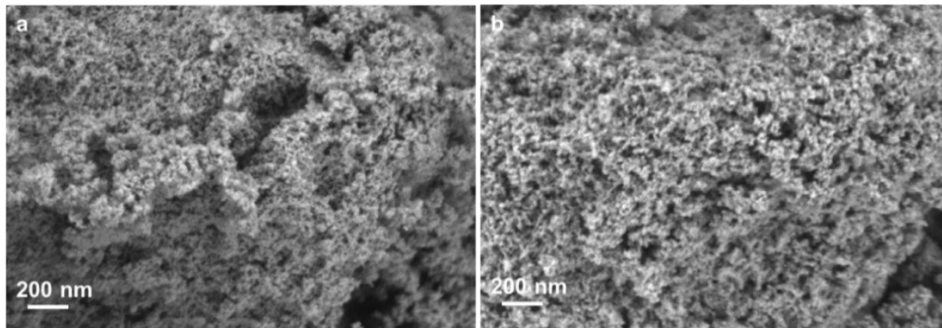


Fig. S2 SEM images of a) ZSO-0.5 and b) ZSO-1.

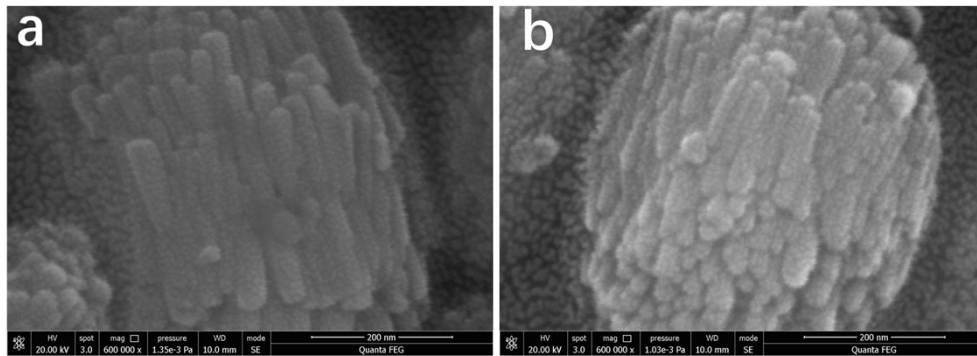


Fig. S3 a, b) SEM images of ZSO-5 with a higher resolution.

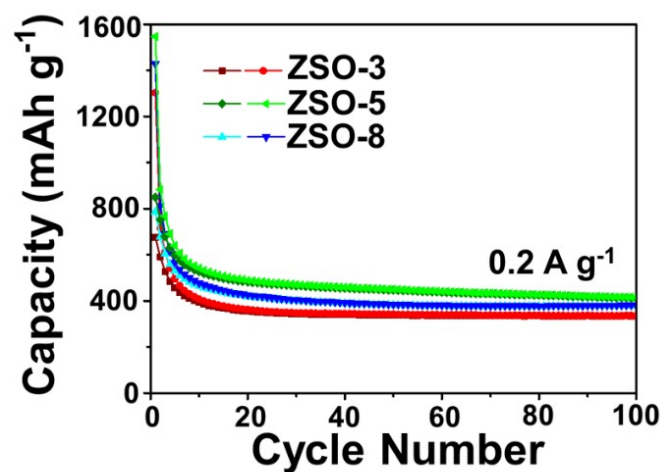


Fig. S4 Cycling performances of Zn₂SiO₄ precursors with reaction time of 3 h (ZSO-3), 5 h (ZSO-5) and 8 h (ZSO-8).

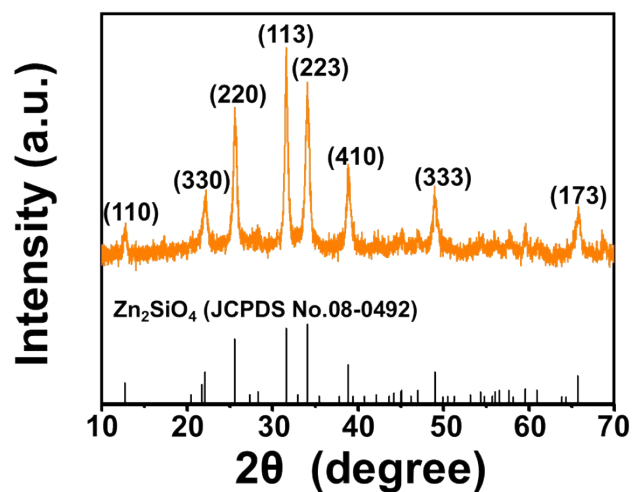


Fig. S5 XRD pattern of Zn₂SiO₄ precursor (ZSO-5).

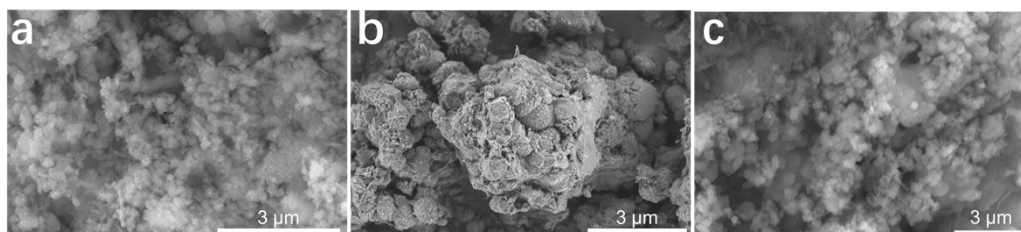


Fig. S6 SEM images of (a) ZSC-1, (b) ZSC-2 and (c) ZSC-3 electrode after 300 cycles.

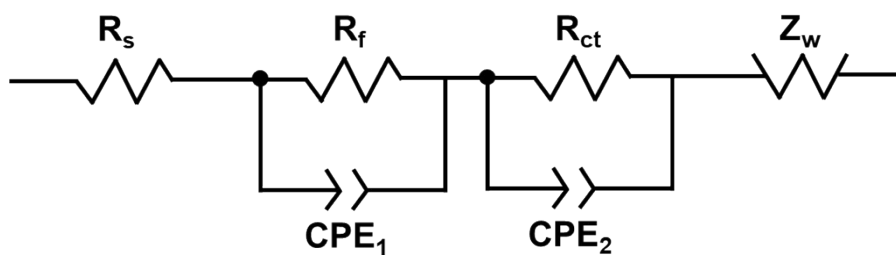


Fig. S7 The equivalent circuit model of porous $\text{Zn}_2\text{SiO}_4@\text{C}$ hybrids.

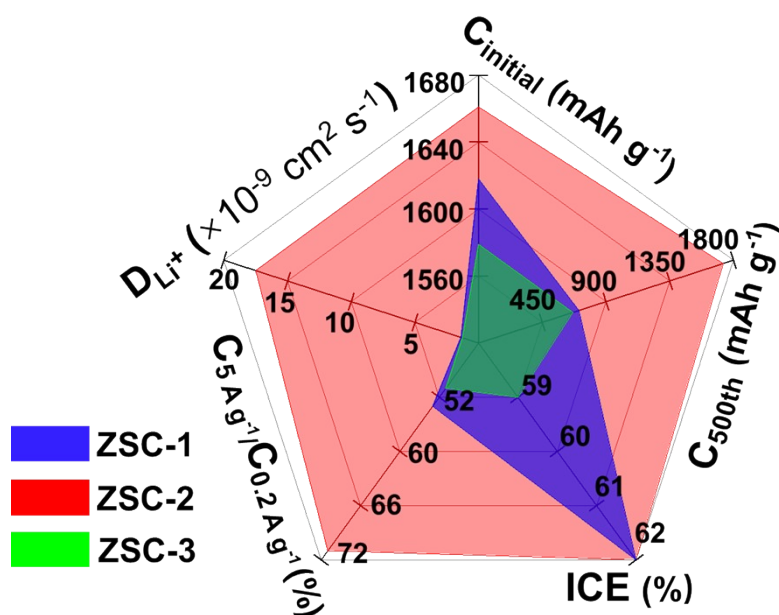


Fig. S8 The comprehensive comparison of electrochemical properties of ZSC-1, ZSC-2 and ZSC-3.

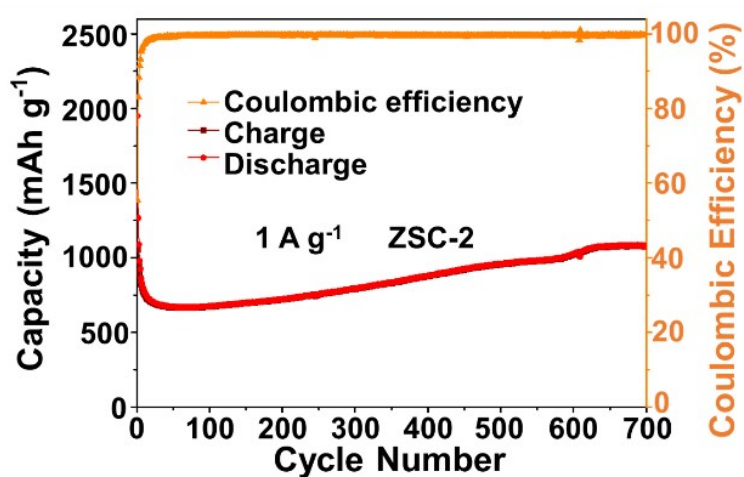


Fig. S9 The long cycling performance of ZSC-2 at 1 A g^{-1} .

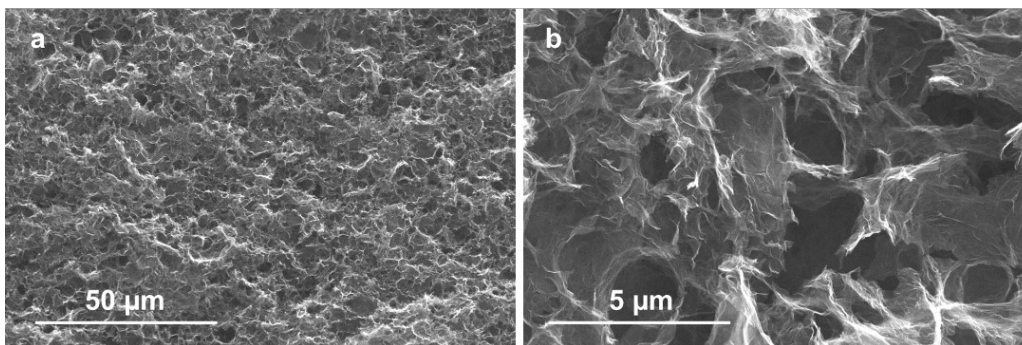


Fig. S10 a,b) SEM images of graphene hydrogel.

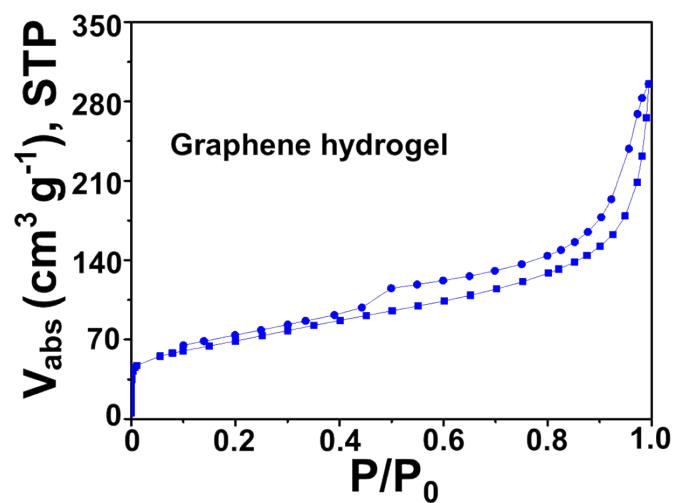


Fig. S11 The nitrogen adsorption-desorption isotherm of graphene hydrogel.

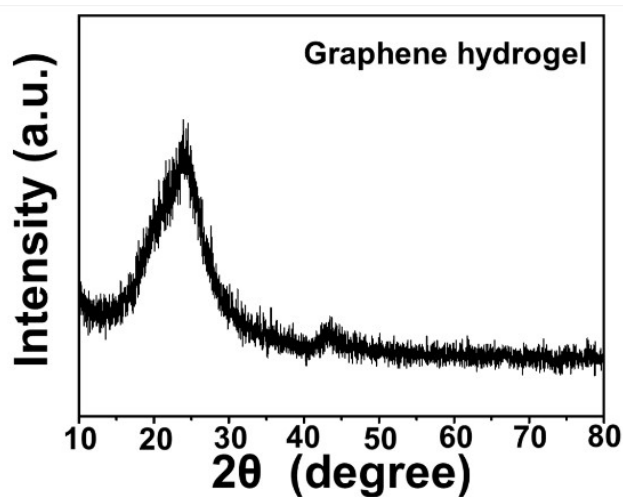


Fig. S12 The XRD pattern of graphene hydrogel.

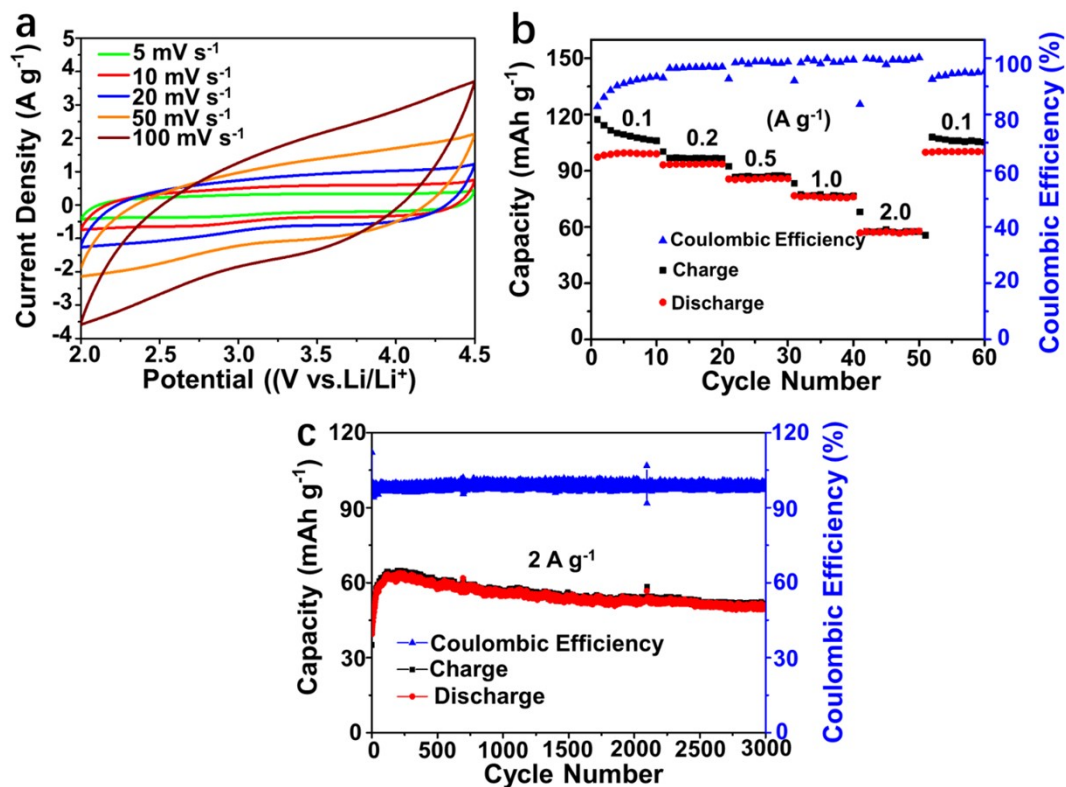


Fig. S13 a) CV curves, b) rate performance and c) cycling performance of graphene hydrogel.

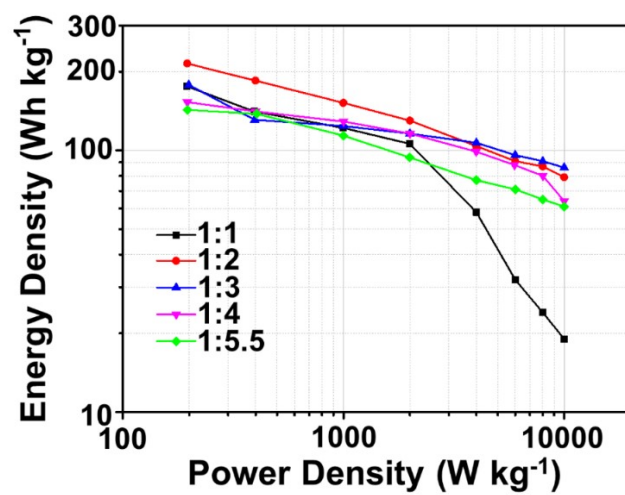


Fig. S14 Ragone plot of ZSC-2//graphene hydrogel based LIC at different mass ratio of anode and cathode.

Table S1. Discharge/charge capacities during the initial cycle, initial coulombic efficiencies (ICE), and discharge capacities after 100 cycles for Zn₂SiO₄ precursors (ZSO-3, ZSO-5 and ZSO-8).

Materials	C _{initial} discharge/charge (mAh g ⁻¹)	ICE (%)	C _{100th} (mAh g ⁻¹)
ZSO-3	1303/676	52	336
ZSO-5	1547/850	55	415
ZSO-8	1429/787	55	384

Table S2. Surface area and pore volume for Zn₂SiO₄@C hybrids (ZSC-1, ZSC-2 and ZSC-3).

Materials	Surface Area (m ² g ⁻¹)	Pore Volume (cm ³ g ⁻¹)
ZSC-1	288	0.21
ZSC-2	535	0.47
ZSC-3	353	0.29

Table S3. The fitting values of R_s, R_f, R_{ct}, C and Z_w.

Sample	R _f (ohm)	R _s (ohm)	CPE ₁ (F)	R _{ct} (ohm)	CPE ₂ (F)	Z _w (S sec ⁵)
ZSC-1	19.5	3.7	8.1×10 ⁻⁵	161.2	3.8×10 ⁻⁷	3.9×10 ⁻³
ZSC-2	4.4	1.0	3.5×10 ⁻³	79.8	1.6×10 ⁻⁶	3.6×10 ⁻³
ZSC-3	3.9	6.3	2.3×10 ⁻⁶	158.3	1.78×10 ⁻⁷	1.1×10 ⁻²

Table S4. Rate performances of some comparable 1D-nanomaterial anodes.

Sample	Structure	Rate capacity(mAh g ⁻¹)			Capacity Ratio		Ref
		0.2	1.0	5.0	$\frac{\text{Capacity}_{\text{at } 1 \text{ A/g}}}{\text{Capacity}_{\text{at } 0.2 \text{ A/g}}}$	$\frac{\text{Capacity}_{\text{at } 5 \text{ A/g}}}{\text{Capacity}_{\text{at } 0.2 \text{ A/g}}}$	
Zn₂SiO₄@C	Submicro-Ellipsoid	1066	984	757	93%	71%	This work
10ZnO-CuO	radial nanorod	386	187	-	48%	-	[2]
Si-Ge	nanowire	1736	801	314	46%	18%	[3]
Mn-PAA/GS/G	nanowire	636	564	391	88%	61%	[4]
Sb ₂ Se ₃ @void@C	nanorod	743	688	-	92%	-	[5]
Sb@NC	nanotube	641	468	426	73%	66%	[6]
Fe-CNT-OCNT	nanotube	~680	576	-	~81%	-	[7]
CoSnO _x @CNF	nanofiber	~810	~690	460	~85%	~57%	[8]

Reference

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