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Supporting Information

Hierarchical N-doped Hollow Carbon Microspheres as Advanced Materials for High-Performance Lithium-Ion Capacitors

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1. Experimental details

1.1 Preparation of NHCM anode material

The hierarchical N-doped hollow carbon microspheres (NHCM) were fabricated by the morphology inheritance strategy. In a typical synthesis, 1.09 g pyromellitic dianhydride (PMDA) and 333.5 μL ethylenediamine (EDA) were added into 30 mL dimethyl formamide (DMF) in order and then stirred vigorously for overnight. The mixture solution was then transferred into an autoclave and heated up to 180 °C for 8 h, 12 h and 16 h, respectively. The as-prepared light-yellow powders were washed with DMF and ethyl alcohol, and then collected after vacuum drying overnight. Finally, the NHCM was obtained by carbonized with 1 °C min^{-1} to 300 °C for 1 h and then 3 °C min^{-1} to 800 °C for 2 h under nitrogen flow. The solvothermal synthesized NHCM with 8 h, 12 h and 16 h were denoted as NHCM-8, NHCM-12 and NHCM-16, respectively.

1.2 Preparation of NPCM-A cathode material

The as-prepared NHCM-12 was mixed with KOH by a mass ratio of 1:4 in deionized water, then followed by evaporating the solution in an oil bath. After that, the dried NHCM-12 /KOH mixture was heated to 800 °C for 1 h with a heating rate of 3 °C min^{-1} under the nitrogen atmosphere. Finally, the sample was washed with 1 M HCl and deionized water, then followed by vacuum drying overnight.

2. Material characterization

The morphologies of the prepared samples and the Energy dispersive X-ray spectroscopy (EDX) of the electrodes were characterized by FESEM (HITACHI S-4800), TEM (FEI, Tecnai-20) and HRTEM (JEOL, JEM-2010), respectively. The XRD measurement was carried out with a Bruker D8 Advance instrument by using Cu Kα radiation. Raman spectra were recorded with HORIBA Scientific Lab RAM HR Raman spectrometer system using a 532.4 nm laser. XPS analysis was performed on a PerkinElmer PHI 550 spectrometer with Al Kα (1486.6 eV). Nitrogen adsorption-desorption isotherms and BET surface area measurements were performed with ASAP-2010 surface area analyzer.

3. Electrochemical devices assembly

3.1 Preparation of anode and cathode half-cells

For anode electrode preparation, the NHCM powders, acetylene black and PVDF binder were homogenously mixed in *N*-methyl pyrrolidinone (NMP) with a mass ratio of 8:1:1. The prepared slurry was pasted on the copper current collector and then dried at 110 °C for 12 h under vacuum. The NHCM-A cathode was prepared similar to the anode, but using the NHCM-A and aluminum foil as the active material and current collector, respectively. The 2016-type coin cells were assembled in an argon-filled glove box by using NHCM or NHCM-A as the working electrode and lithium metal as the counter and reference electrode. 1 M $LiPF_6$ was dissolved in volumetric ratio of a 1:1:1 mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) was used as the electrolyte and polypropylene was used as the separator.

3.2 Preparation of lithium-ion capacitors

Dual-carbon based LICs (NHCM-12//NHCM-A) were assembled with pre-lithiated NHCM-12 anode and NHCM-A cathode in the same organic electrolyte as half-cells.

The anode and cathode with the mass ratios of 1:1, 1:2, 1:3, and 1:4 were investigated in this study. Typically, the optimal LIC mass loading of anode and cathode were 0.9 mg cm^{-2} and 2.7 mg cm^{-2}, respectively. The energy densities and current densities were calculated based on the total mass of the active materials.

4. Electrochemical measurements

All of electrochemical measurements and charge storage mechanism studies were carried out at room temperature. In brief, the cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) was performed on the electrochemical workstations (CHI 760E). Galvanostatic charge–discharge and cycle-life tests were carried out by using CT20001A cell test instrument (LAND Electronic Co.). Before *ex-situ* EDX characterization, the cells were disassembled, electrodes were wised with DMC and then naturally drying in glove box.

The specific capacitance (C, F g^{-1}), energy density (E, Wh kg^{-1}) and power density (P, W kg^{-1}) of LICs can be calculated according to the following equations:

$$E = \int_{t1}^{t2} IVdt = \frac{1}{2}C(V_{max} + V_{min})(V_{max} - V_{min})$$

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

$$P = \frac{E}{t}$$

Where $V_{\max}$ and $V_{\min}$ are the initial and final discharge voltages, ΔV is the difference value of the $V_{\max}$ and $V_{\min}$, I is the current density, m is the total mass of the active material within both electrodes and t is the discharge time.

5. Density functional theory (DFT) computational details

DFT calculations were implemented in Vienna *ab initio* simulation package (VASP).[1] Generalized gradient approximation (GGA) with the function of Perdew–Burke–Ernzerhof (PBE) was employed to describe the electron interaction energy of exchange correlation.[2] Grimme's semi–empirical DFT–D3 scheme was used in the computations to produce a better description of the Van der Waals interaction in a long range.[3] The plane–wave basis set with an energy cutoff of 450 eV in all calculations. The Hellmann–Feynman forces convergence criterion on the atoms was set to be lower than 0.02 eV $Å^{-1}$ during geometrical optimization. Tolerance of self-consistency calculation was achieved at least 10^{-1} eV in the total energy. The Brillouin zone was sampled by Monkhorst–Pack method with 3×3×1 k-points for the single-layer model.[4] A vacuum layer of 13 Å along the c axis direction normal to the sheet was chosen to avoid periodic interactions.

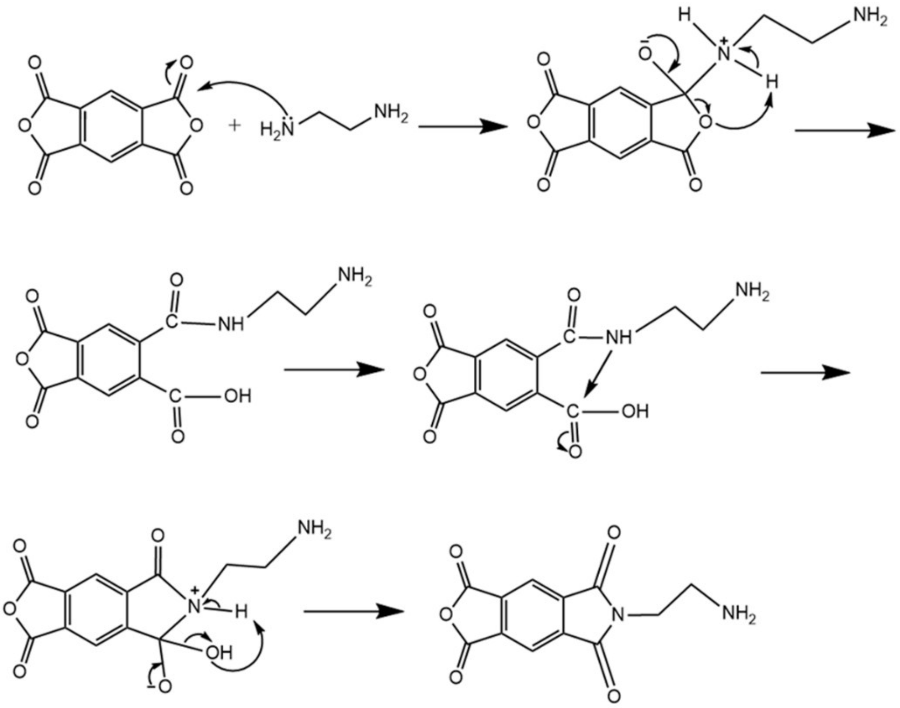

Fig. S1 The reaction mechanism of one-molecule polyimide self-assembled process.

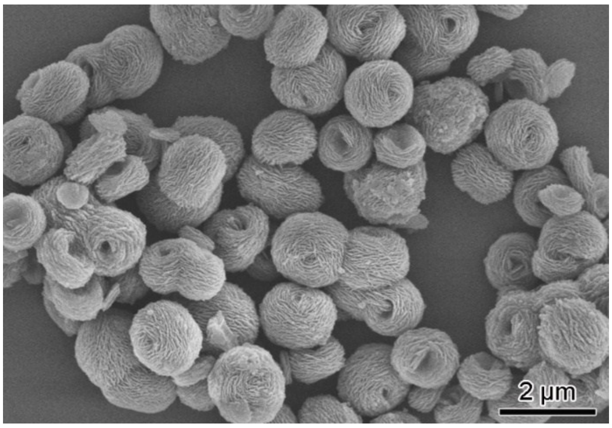

Fig. S2 The SEM image of polyimide precursor for NHCM-12 anode.

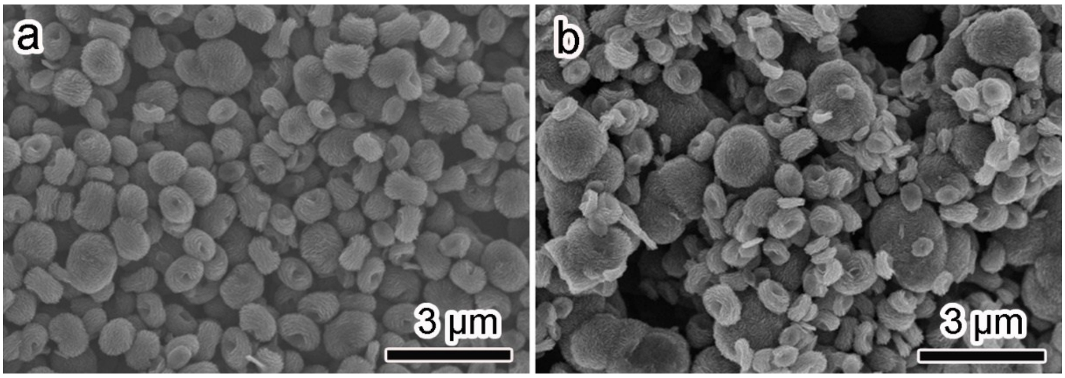

Fig. S3 The SEM images of a) NHCM-8 and b) NHCM-16 anode.

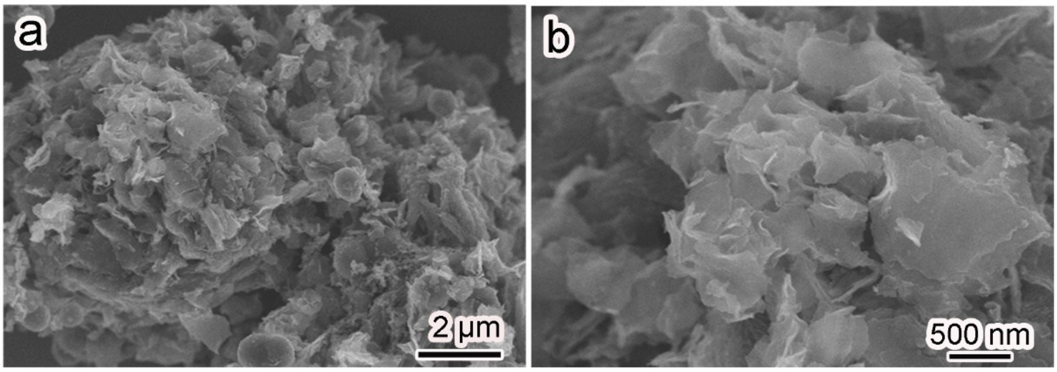

Fig. S4 (a,b) The SEM images of polyimide-derived carbon using methylpyrrolidone (NMP) as the reaction solvent.

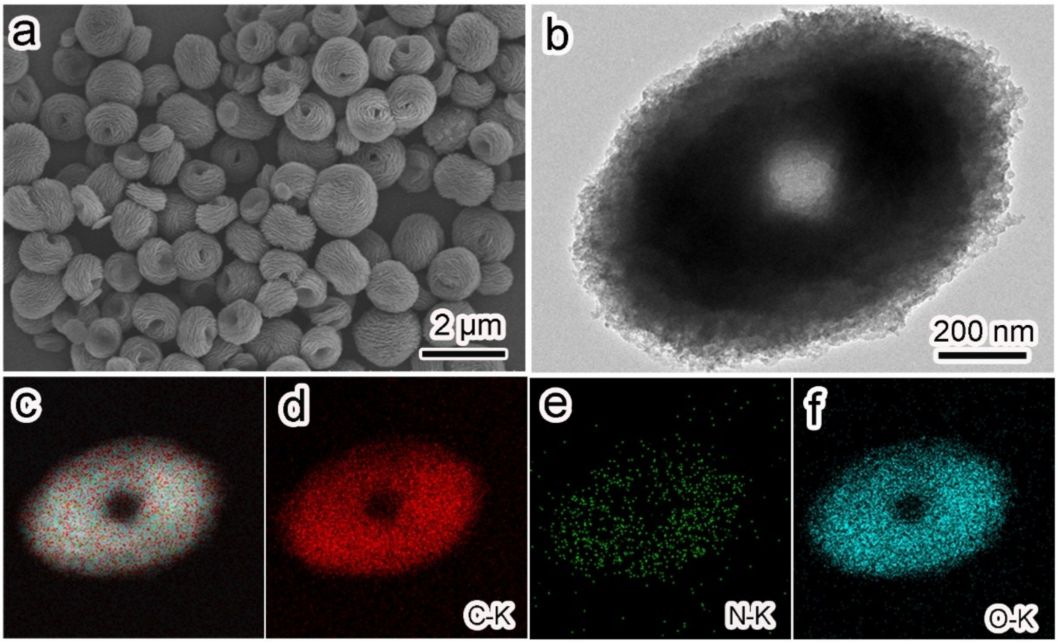

Fig. S5 (a) SEM image and (b) TEM image of the NHCM-A cathode. (c) STEM images of NHCM-A with the corresponding (d) C, (e) N and (f) O elements mapping.

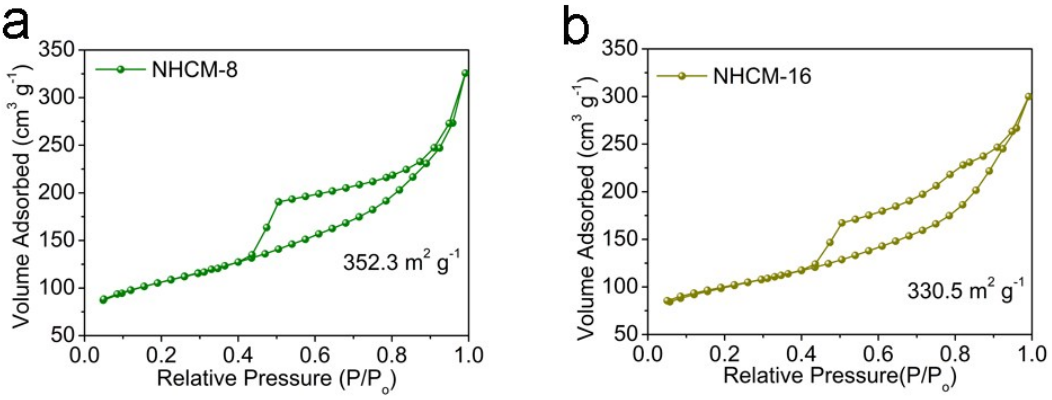

Fig. S6 N_2 adsorption–desorption isotherms of the (a) NHCM-8 and (b) NHCM-16, respectively.

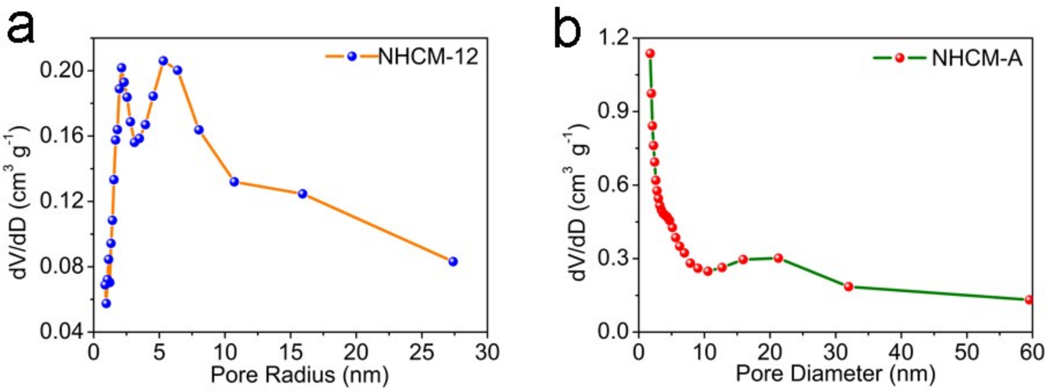

Fig. S7 Pore size distribution curves of (a) NHCM-12 anode and (b) NHCM-A cathode, respectively.

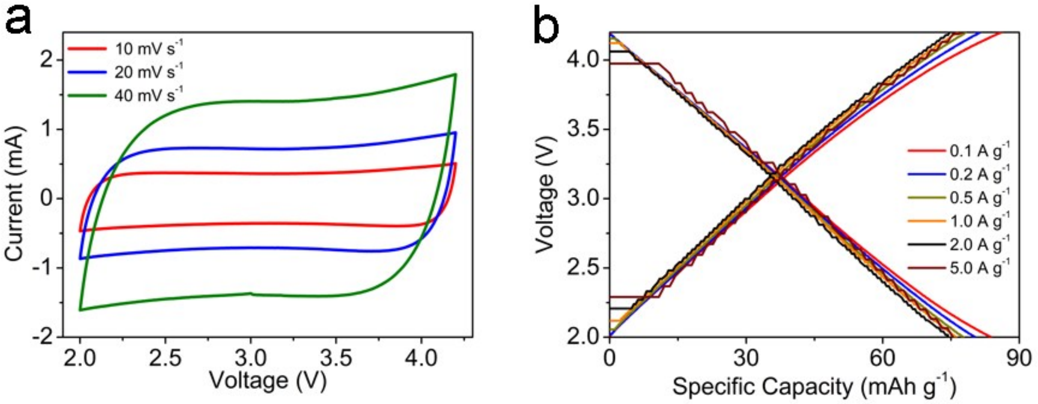

Fig. S8 (a) CV curves and (b) galvanostatic charge-discharge curves of the NHCM-A.

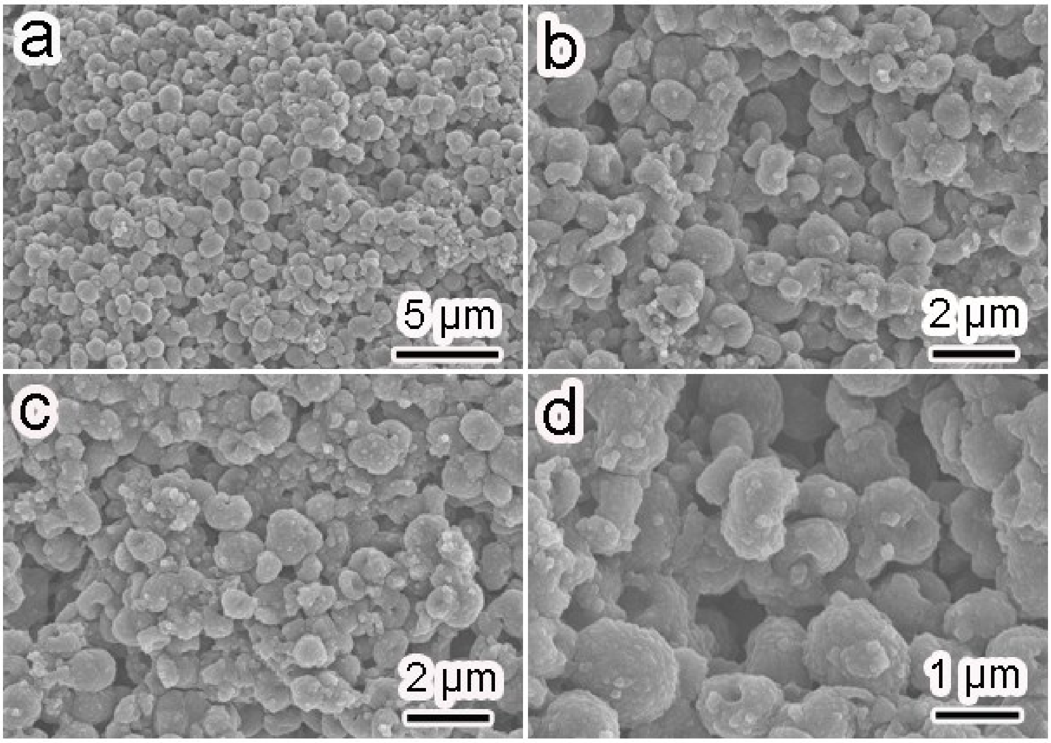

Fig. S9 (a-d) SEM images of the NHCM-12 electrode after 2000 cycles at 1A g^{-1}.

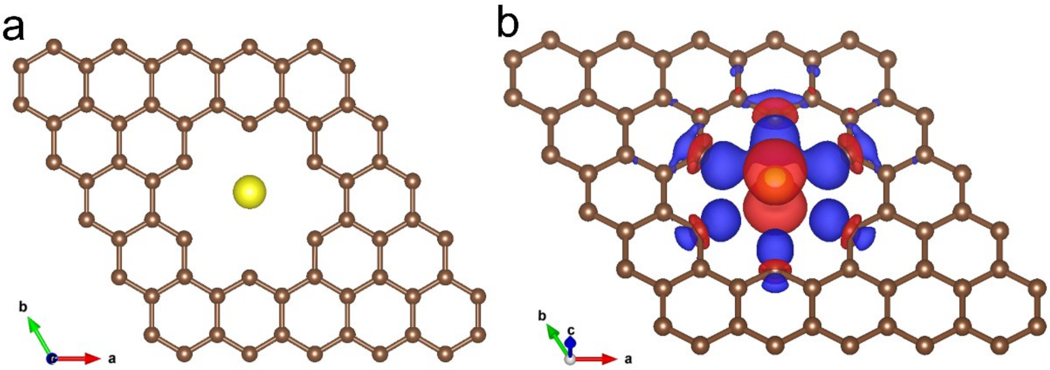

Fig. S10 (a) DFT calculations with the models of DCs. (b) Charge density difference of a Li atom adsorbed on DCs

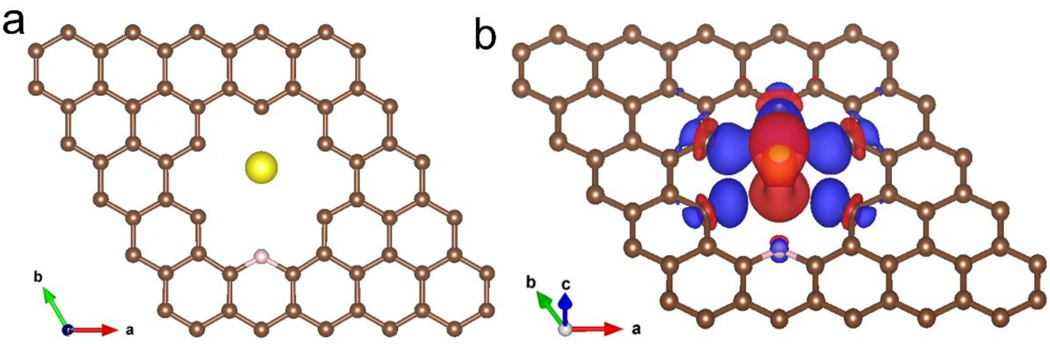

Fig. S11 (a) DFT calculations with the models of OCs. (b) Charge density difference of a Li atom adsorbed on OCs

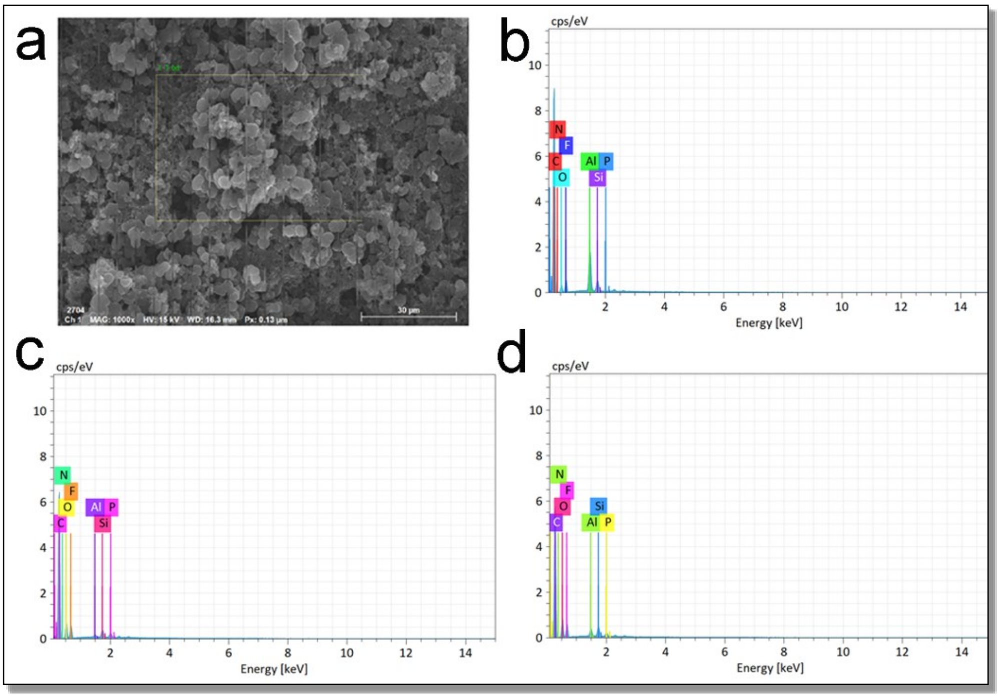

Fig. S12 The EDX images of (a,b) pristine state, (c) initial charge and (d) initial discharge state for NHCM-A electrode.

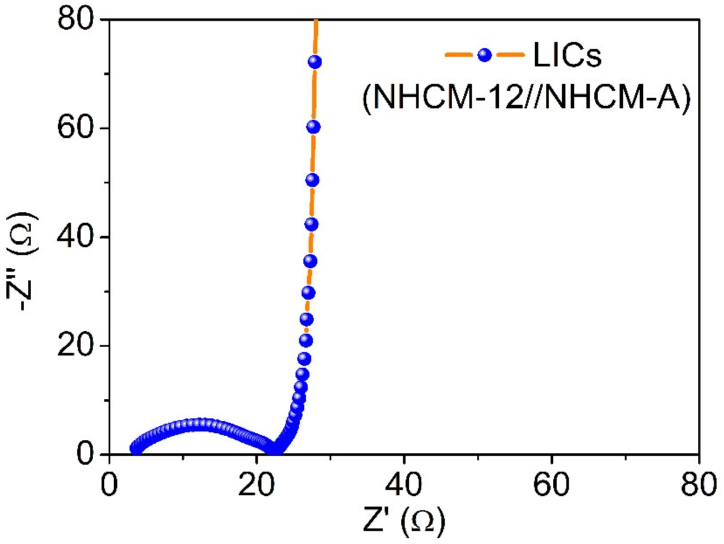

Fig. S13 Nyquist plots for optimal LIC (NHCM-12//NHCM-A).

Table. S1 The different binding energy values obtained from the DFT calculations.

Samples	Total energy (eV)	Substrate energy (eV)	Li atom energy (eV)	Binding energy (eV)
PCs	-668.07	-666.47	-0.03	-1.57
QCs	-665.86	-664.74	-0.03	-1.09
PRCs	-609.47	-603.88	-0.03	-5.56
PDCs	-599.26	-593.90	-0.03	-5.33
DCs	-597.40	-592.19	-0.03	-5.18
OCs	-597.73	-592.56	-0.03	-5.14

Table. S2 The EDX results of all the atoms percent with pristine, initial charge and initial discharge states for NHCM-A electrode.

Chemical element	Pristine state (Atom %)	Initial charge (Atom %)	Initial discharge (Atom %)
C	85.7	76.3	73.7
N	1.2	1.7	1.6
O	5.5	14.1	2.5
Al	2.6	0.2	0.1
Si	0.7	0.7	0.1
F	4.2	6.7	1.4
P	0	0.4	0.1

Table. S3 Summary of electrochemical characteristics of reported hybrid LICs and our LIC (NHCM-12//NHCM-A).

LICs type (anode//cathode)	Voltage range (V)	Max energy density	Max power/energy density	Max Cycle number	Cycle stability (%)	Ref.
$Li_4Ti_5O_{12}$//AC	0~3	94	3000/32	500	87	[5]
$Li_4Ti_5O_{12}$//MOF-C	1~3	65	10000/9	10000	82	[6]
$H_2Ti_8O_{17}$//AC	1~3	94	15000/33	3000	78.8	[7]
TiO_2//GO	1~3	42	8000/9	100	80	[8]
T-Nb_2O_5//GO	0.5~3.0	47	18000/47	2000	93	[9]
m-Nb_2O_5//MSP-20	1~3.5	63	16528/5	1000	100	[10]
$TiNb_2O_7$//GO	0~3	74	7500/35	3000	81.3	[11]
$TiNb_2O_7$ //CF	2.8~4.2	100	5464/20	1500	77	[12]
CPIMS//AC	2~4	29	6940/13	5000	97.1	[13]
TiC//AC	0~4.5	102	67500/23	5000	82	[14]
NbN//AC	2~4	123	2000/98	1000	81.7	[15]
SnO_2//AC	0.5~4	110	2950/48	2000	80	[16]
Ti_2C(Mxene)//YP17	1~3.5	50	930/30	1000	85	[17]
VS_2//rGO	0.5~4	121	3600/29	1000	79	[18]
MoS_2//NPC	0~4	156	8314/97	2000	78	[19]
MnO@C//PC-75	0.1~4	118	10250/28	3000	76	[20]
Fe_3O_4@//Ppy@CNT	1~4	101	17186/70	2000	79.5	[21]

Fe_3O_4@GO//3D GO	1~4	147	2587/86	2000	70	[22]
LTO@HG//HG	1.5~3.0	117	19700/43	2000	81.7	[23]
MnO@C//AC	1.0~4	100	20000/30	5000	70	[24]
ɣ-$Li_xV_2O_5$//AC	0~2.3	55	280/44	400	86	[25]
α-Fe_2O_3@CG//CG	1~4	121	18000/60	2000	87	[26]
Mn_3O_4-G//APDC	1~4	97	6250/5	1000	76.8	[27]
BNC//Graphite	1~4	116	10000/54	2000	73.6	[28]
T-Nb_2O5@NC//AC	0.5~3	50	8750/	1000	91.1	[29]
NQD-NC//AC	0.5~4	77	11250/22	4500	85	[30]
NHCM-12//NHCM-A	0.1~4	162	10250/103	5000	86.2	This work

* The units of power density and energy density are Wh kg^{-1} and W kg^{-1}, respectively.

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