Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Electronic Supporting Information (ESI)

Controllable synthesis and electrochemical capacitor performance of MOF-derived MnO_x/N-doped carbon/MnO_2 composites

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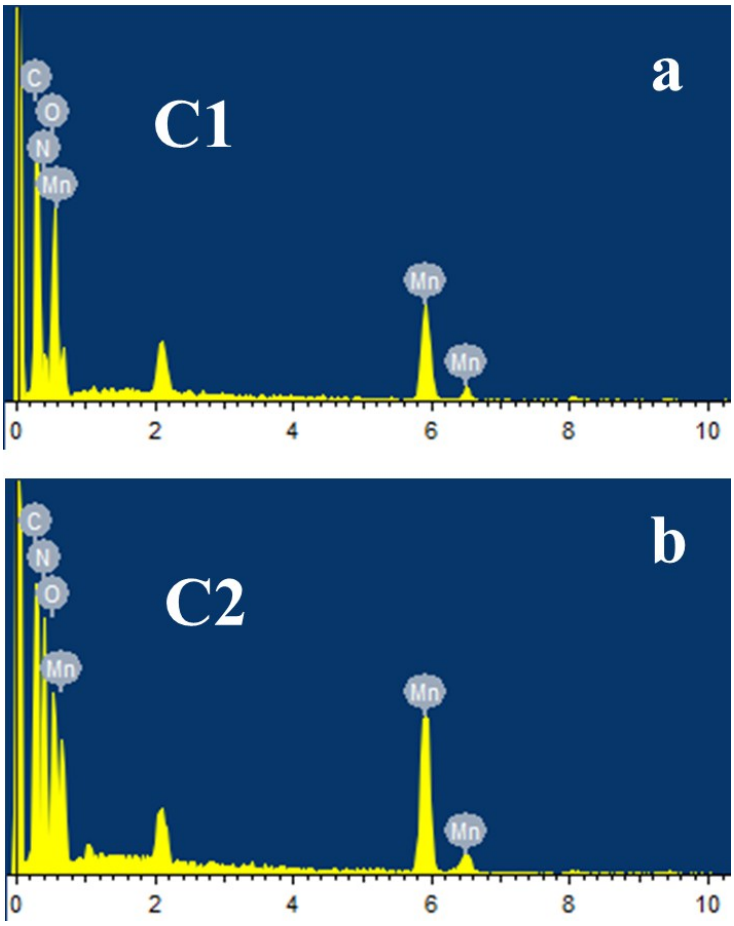

Fig. S1. Structural characterization. EDX patterns of MOF-derived C1 and C2 sample.

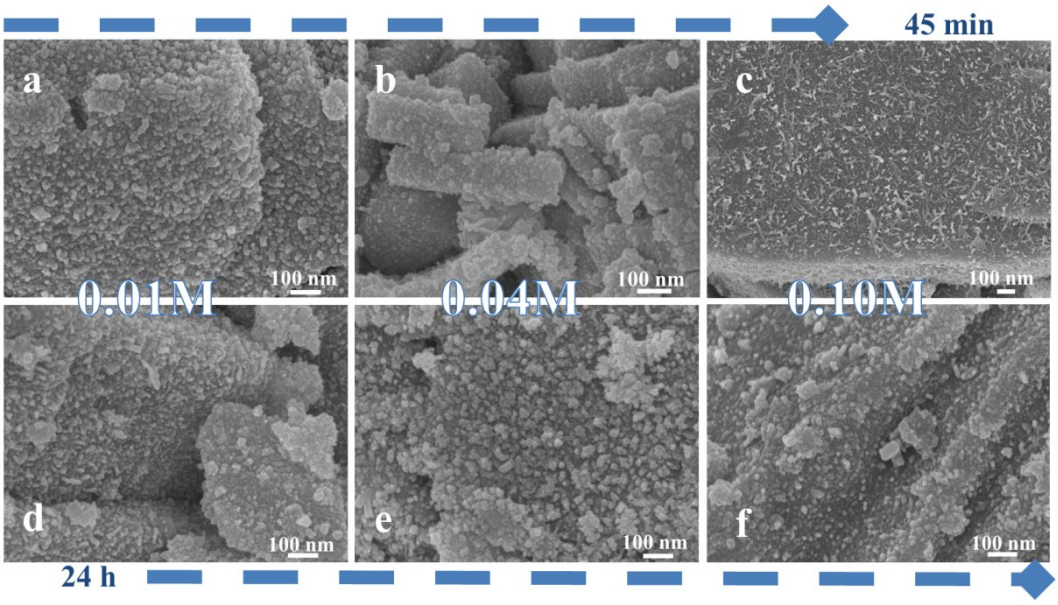

Fig. S2. Morphology characterization of C2-*x*-*y* samples. (a-c) SEM images of C2-*x*-45min sample. (d-f) SEM images of C2-*x*-24h sample.

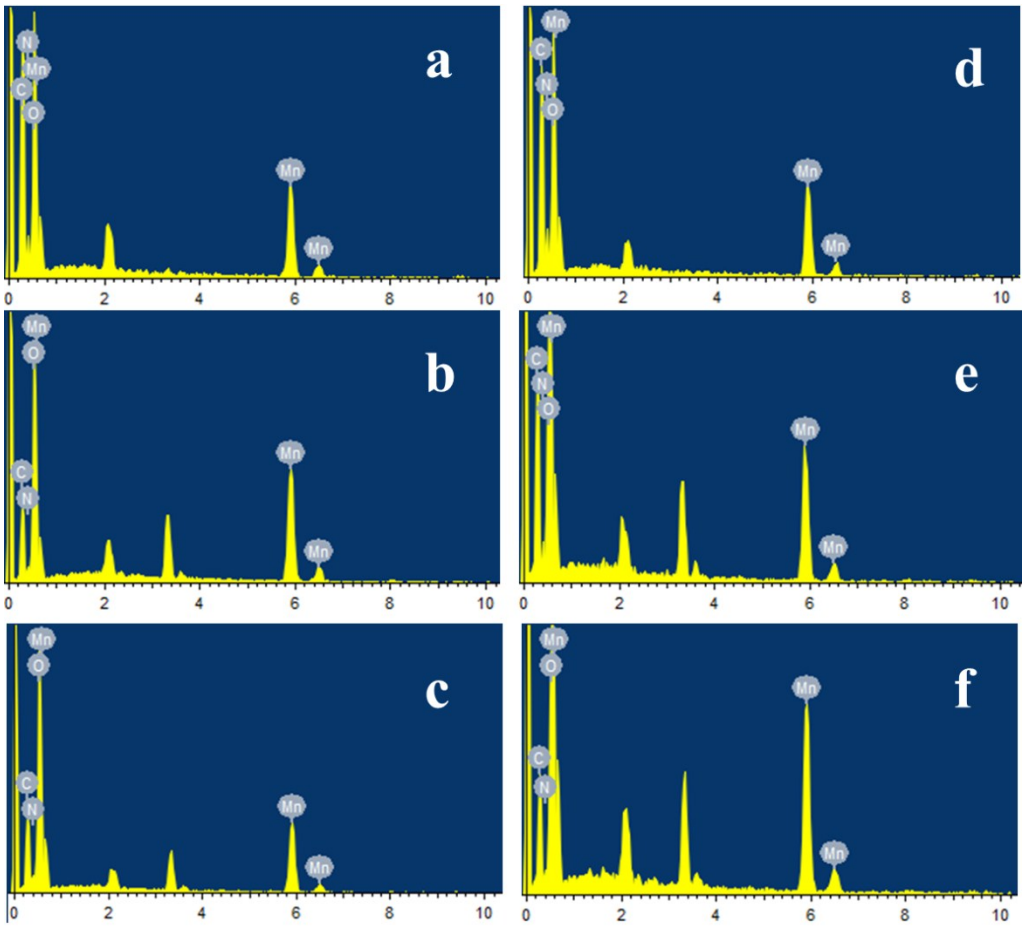

Fig. S3. Structural characterization of C1-derived samples. (a-c) EDX patterns of C1-*x*-45min samples. (d-f) EDX patterns of C1-*x*-24h samples.

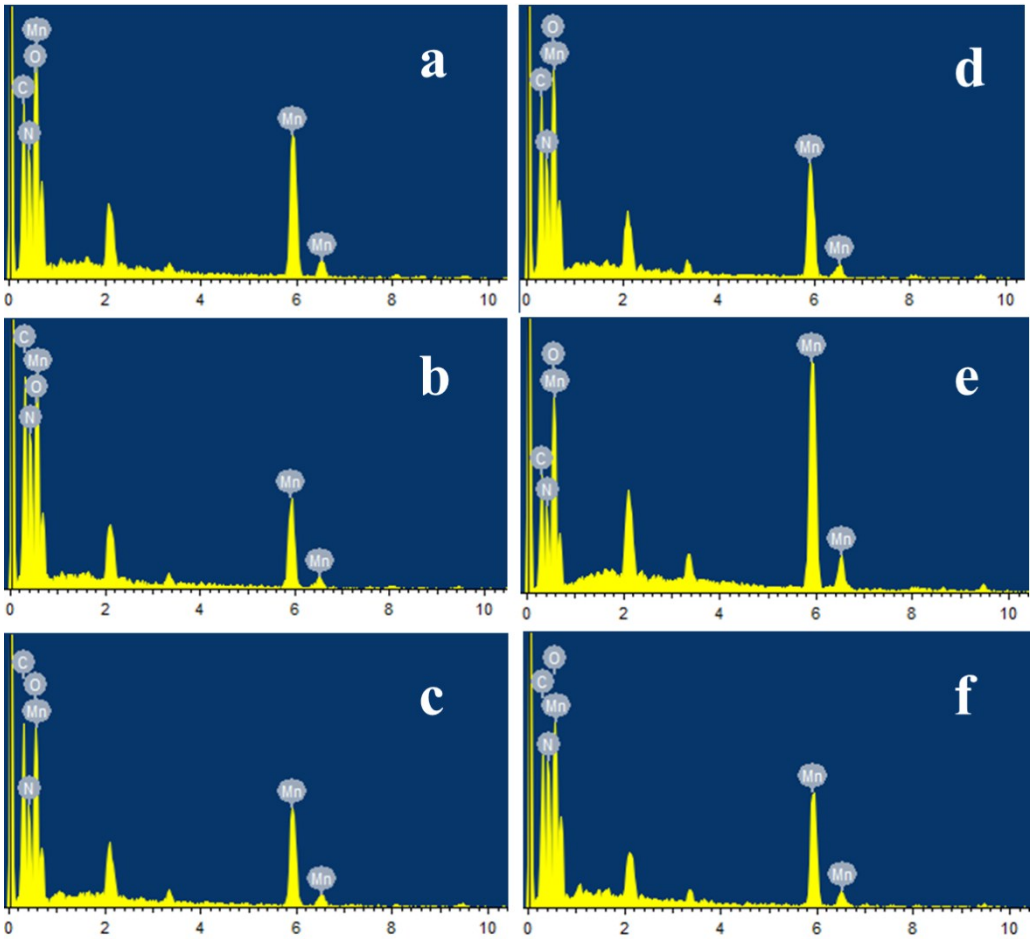

Fig. S4. Structural characterization of C2-derived samples. (a-c) EDX patterns of C2-*x*-45min samples. (d-f) EDX patterns of C2-*x*-24h samples.

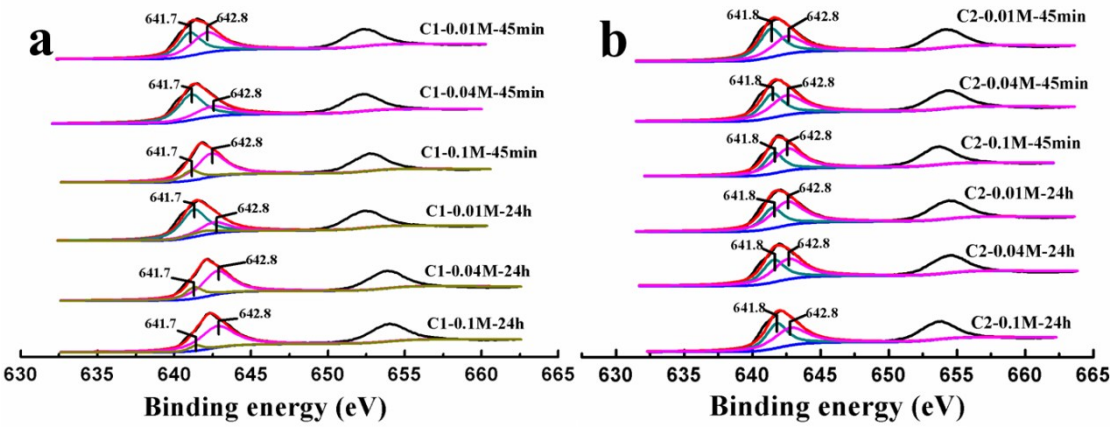

Fig. S5. XPS characterization of C1 and C2-derived samples. **(**a) Deconvolution of the Mn 2p region of C1-*x*-*y* samples. (b) Deconvolution of the Mn 2p region of C2-*x*-*y* products.

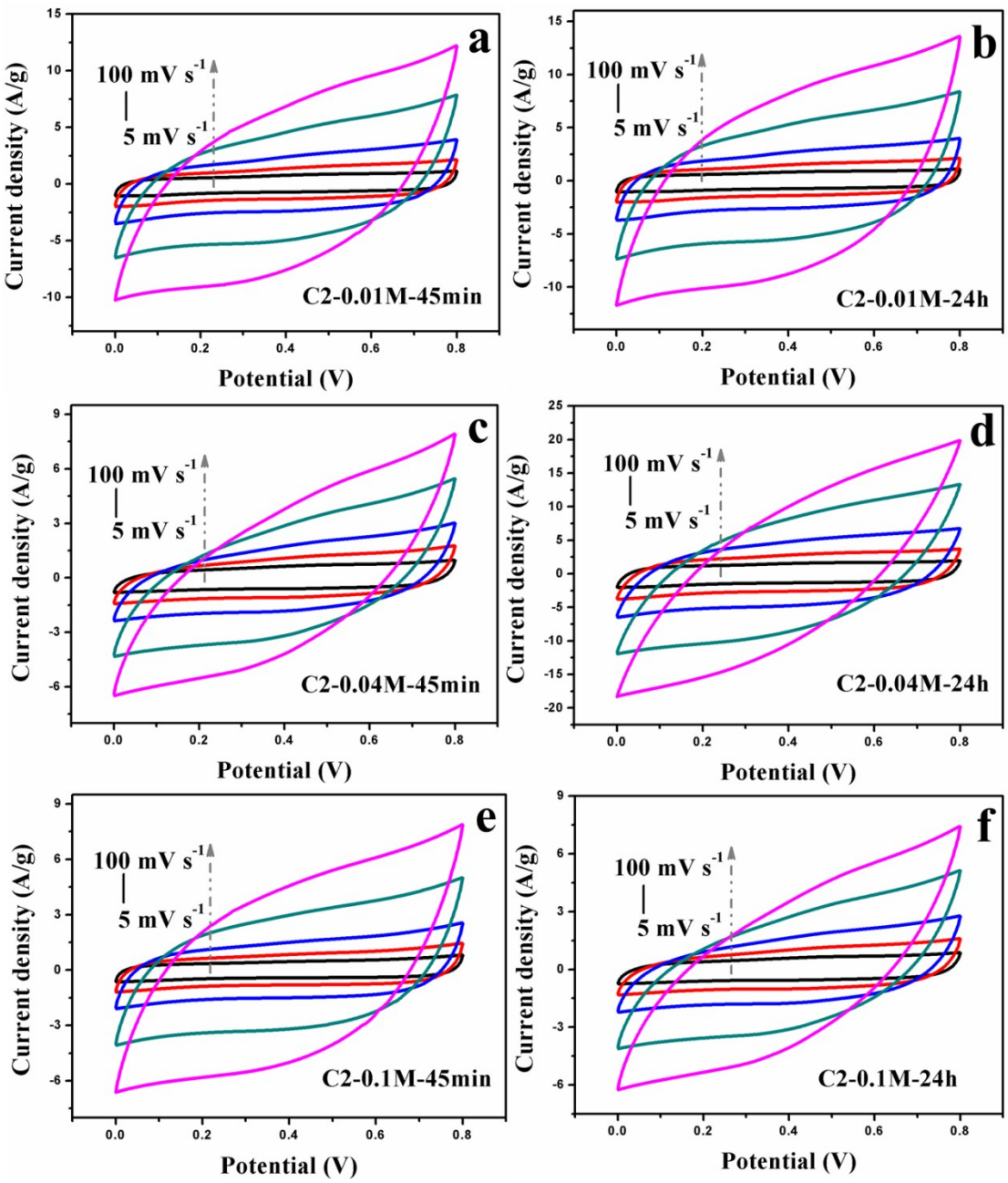

Fig. S6. Electrochemical performance. (a-b) CV curves of as-synthesized C2-0.01M-*y* electrodes at different scan rates. (c-d) CV curves of as-synthesized C2-0.04M-*y* electrodes at different scan rates. (e-f) CV curves of as-synthesized C2-0.10M-*y* electrodes at different scan rates.

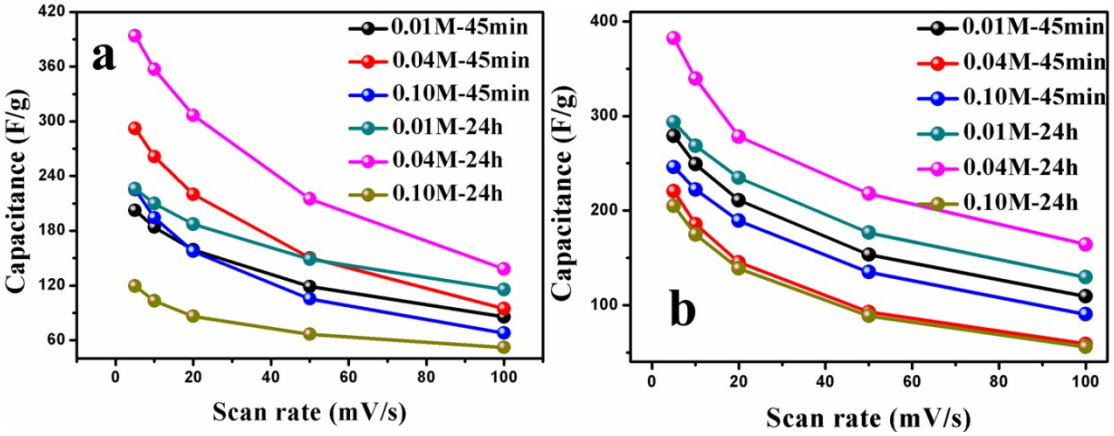

Fig. S7. CV Comparison. (a) The specific capacitances of C1-*x*-*y* electrodes calculated according to the CV curves at different scan rates. (b) The specific capacitances of C2-*x*-*y* electrodes calculated according to the CV curves at different scan rates.

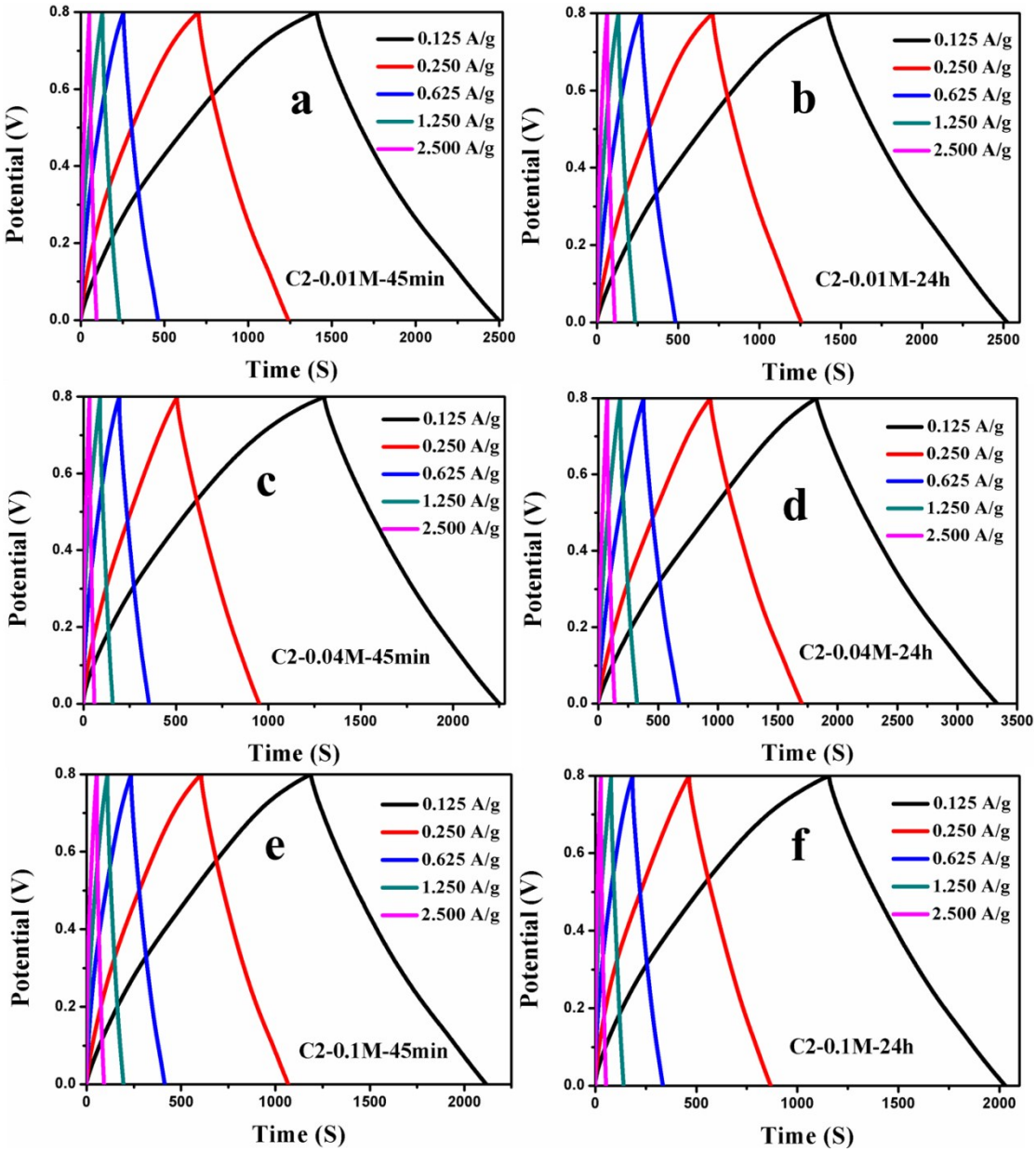

Fig. S8. Charge-discharge curves. (a-b) CP curves of as-synthesized C2-0.01M-*y* electrodes at different current densities. (c-d) CP curves of as-synthesized C2-0.04M-*y* electrodes at

different current densities. (e-f) CP curves of as-synthesized C2-0.10M-*y* electrodes at different current densities.

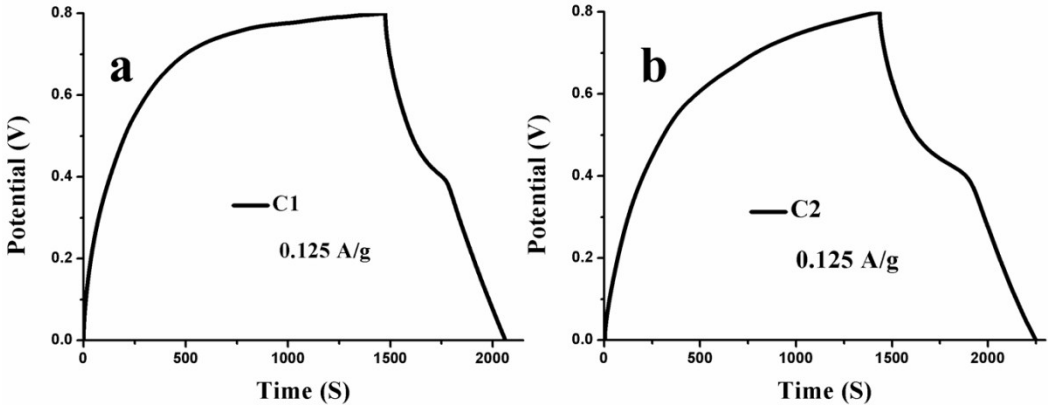

Fig. S9. CP curves of electrode C1 and C2 at a current density of 0.125 A g^{-1}.

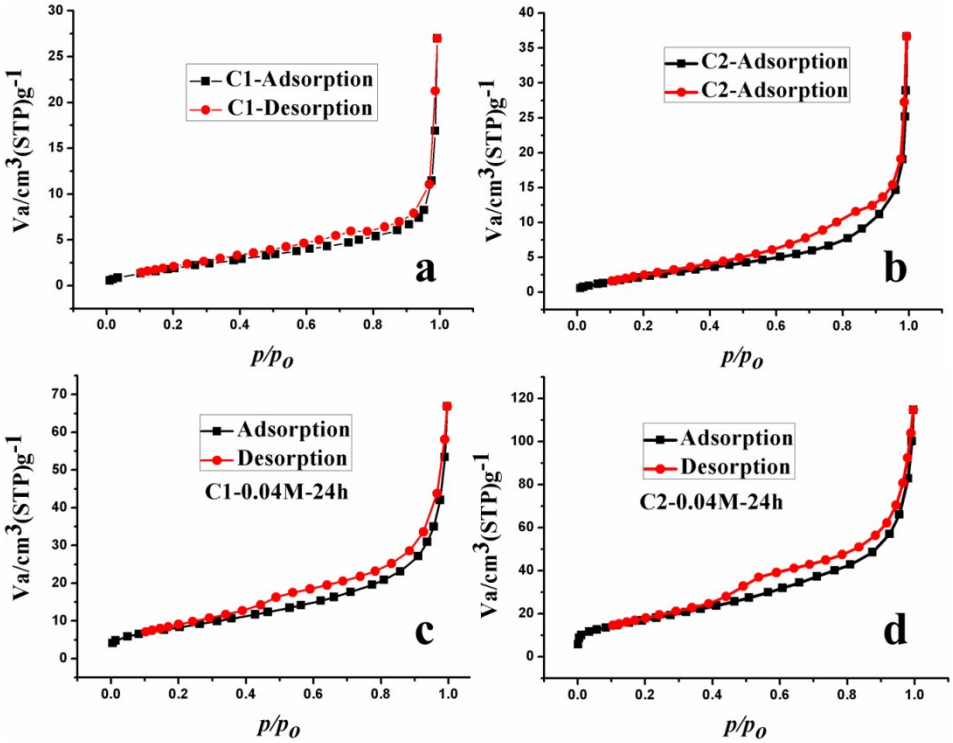

Fig. S10. N_2 adsorption-desorption curves for C1 (a), C2 (b), C1-0.04M-24h (c) and C2-0.04M-24h (d) respectively.

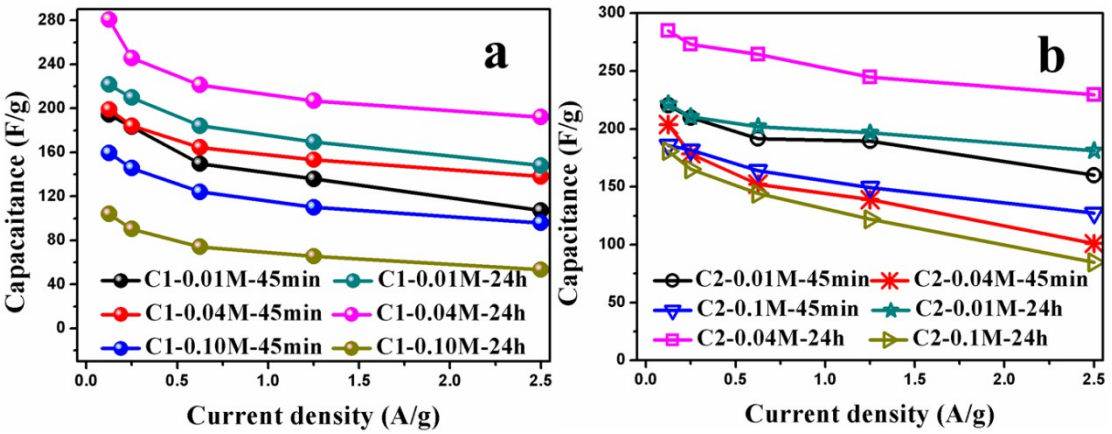

Fig. S11. CP comparison. (a) Specific capacitance variations of C1-*x*-*y* electrodes at different current densities. (b) Specific capacitance variations of C2-*x*-*y* electrodes at different current densities.

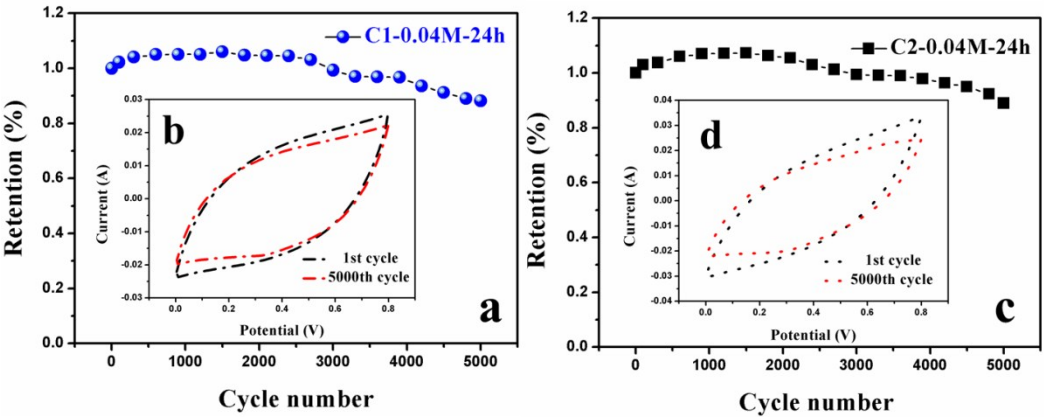

Fig. S12. Cycling-life test. a) Endurance test for as-prepared C1-0.04M-24h electrode at a constant scan rate of 100 mV s^{-1}. b) Compared CV curves before and after 3000 cycles. (c-d) Cycling test and Compared CV curves for C2-0.04M-24h electrode at a scan rate of 100 mV s^{-1}.

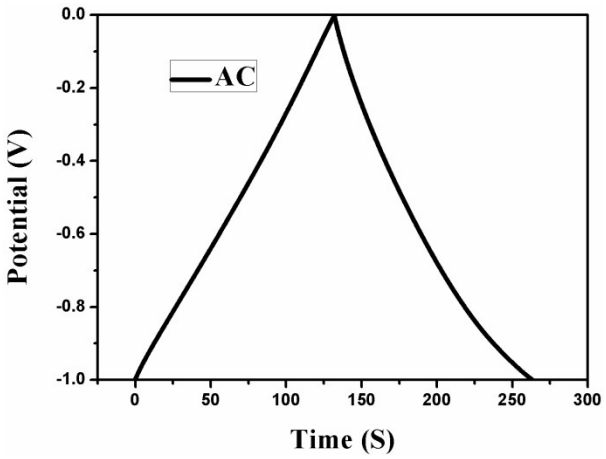

Fig. S13. CP curve of AC at a current density of 1.0 A g^{-1}.

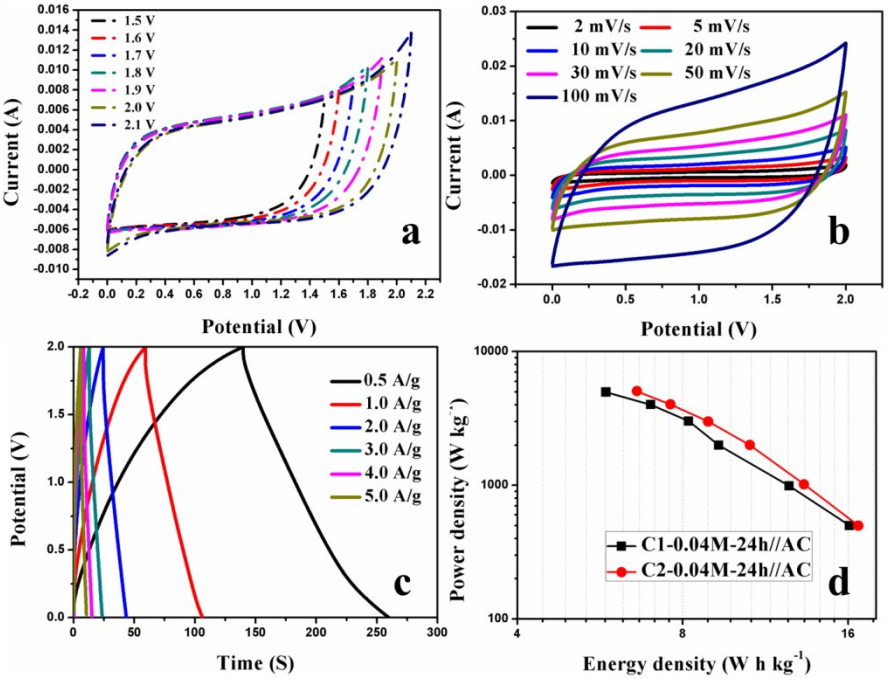

Fig. S14. CV curves of (a) C2-0.04M-24h//AC ASC device ranged in different potential window at a scan rate of 30 mV s^{-1}. (b) CV curves of C2-0.04M-24h//AC ASC device at different sweep rates. (c) CP curves of C2-0.04M-24h//AC ASC device at different current densities. (d) Ragone plots of energy density and power density of C1-0.04M-24h//AC and C2-0.04M-24h//AC.

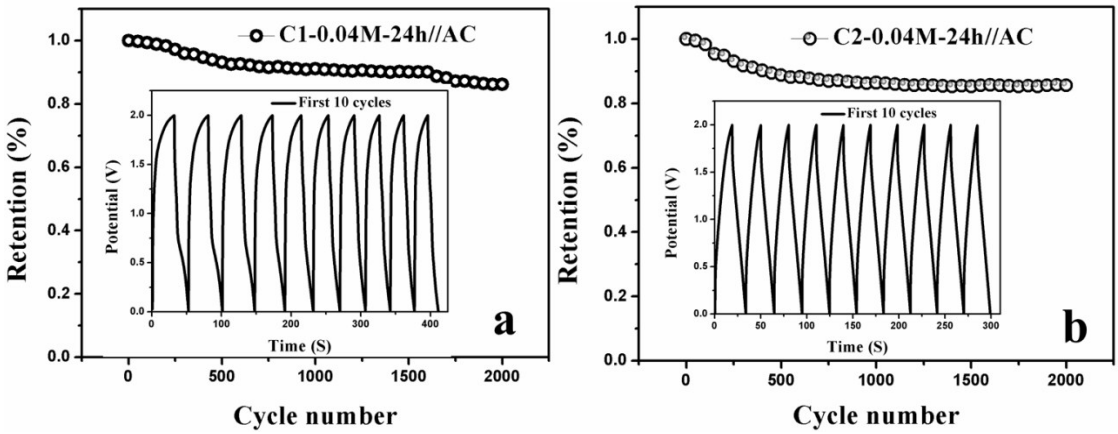

Fig. S15. Endurance test for C1-0.04M-24h//AC and C2-0.04M-24h//AC ASC devices at a current density of 2 A g^{-1}. Inset: the first ten continuous cycles.

Table S1. The content of Mn and C of C2-*x*-*y* tested from XPS spectra

Samples	Element (atomic concentration %)	
	Mn	C
C2	5.59	36.82
C2-0.01M-45min	21.84	22.38
C2-0.04M-45min	22.11	20.08
C2-0.10M-45min	22.82	19.11
C2-0.01M-24h	20.02	21.27
C2-0.04M-24h	22.17	19.52
C2-0.10M-24h	24.30	18.82

Table S2. Summary of N-doped materials reported in references.

Sample	**N (At%)**	**Reference**	**Method**
C1-0.01M-45min	12.11	this work	MOF pyrolysis
C2-0.01M-45min	14.79		
C1	17.92		
C2	24.19		
N-Graphene	0.11-1.35	35	N plasma treatment
N-ZnO	5.0	36	Solvothermal
N-Carbon film	12.0	37	Sputtering
N-doped carbon	0.68-7.64	38	Precursor
N,S-carbon	0.1-2.9	39	NH_3 treatment

Table S3. The proportions of carbon/nitrogen (C/N) determined from XPS spectra

Samples	C/N	Samples	C/N
C1-0.01M-45min	2.97	C2-0.01M-45min	1.57
C1-0.04M-45min	3.90	C2-0.04M-45min	1.86

C1-0.10M-45min	5.00	C2-0.10M-45min	1.88
C1-0.01M-24h	3.96	C2-0.01M-24h	1.77
C1-0.04M-24h	6.76	C2-0.04M-24h	1.84
C1-0.10M-24h	7.96	C2-0.10M-24h	2.48
C1	2.25	C2	1.52

Table S4. The conductive data for solid samples through Four-point Probe.

Samples+AB	d (cm)	σ (S·cm^{-1})	Proportion	N (At%)	C/N ratio
C1-0.01M-45min	0.54	9.71×10^{-3}	75%:15%	12.11	2.97
C1-0.04M-45min	0.50	4.00×10^{-2}	75%:15%	8.53	3.90
C1-0.10M-45min	0.47	7.25×10^{-3}	75%:15%	5.07	5.00
C1-0.01M-24h	0.46	1.64×10^{-2}	75%:15%	8.54	3.96
C1-0.04M-24h	0.50	0.156	75%:15%	3.50	6.76
C1-0.10M-24h	0.47	9.01×10^{-3}	75%:15%	2.58	7.96
C2-0.01M-45min	0.54	1.98×10^{-3}	75%:15%	14.79	1.57
C2-0.04M-45min	0.50	0.152	75%:15%	10.80	1.86
C2-0.10M-45min	0.54	1.45×10^{-2}	75%:15%	10.19	1.88
C2-0.01M-24h	0.47	0.258	75%:15%	12.04	1.77
C2-0.04M-24h	0.47	0.341	75%:15%	10.62	1.84
C2-0.10M-24h	0.50	2.60×10^{-2}	75%:15%	7.60	2.48
acetylene black (AB)	1.48	0.140	/	/	/

Table S5. Summary of electrochemical measurements in recent papers for MnO_x electrodes.

Sample of MnO_x	Electrolyte	Measurement protocol	Maximum capacitance (F/g)	Capacitance retention after cycle test	Ref.
Mn_3O_4 film	1 M Na_2SO_4	CV (υ = 10 mV/s)	193	/	41a
graphene / Mn_3O_4	1 M Na_2SO_4 6 M KOH	CV (υ = 5 mV/s)	175 256	/	41b
Mn_3O_4 powder	2 M KCl	CV (υ = 5 mV/s)	148	almost 100% after 400 cycles	42
MWCNT/ Mn_3O_4 film	0.5 M Na_2SO_4	CV (υ = 2 mV/s)	143	81% after 1000 cycles	43
Mn_3O_4@C NWs	1 M Na_2SO_4	CV (υ = 2.5 mV/s)	197	92% after 3000 cycles	44
MC-CS-MnO_2	1 M Na_2SO_4	CP (*i* = 0.5 A/g)	326	>100% after 1000 cycles	45a
GO-DE@MnO_2	1 M Na_2SO_4	CP (*i* = 2.0 A/g)	152.5	83.3% after 2000 cycles	45b
MnO_2/CNT	1 M Na_2SO_4	CP (*i* = 0.5 A/g)	370	about 100% after 4000 cycles	46a
PDA@MnO_2	1 M Na_2SO_4	CP (*i* = 2.0 A/g)	193	81.2% after 2500 cycles	46b
CF@MnO_2	0.5 M Na_2SO_4	CP (*i* = 1.0 A/g)	321.3	99.7% after 3000 cycles	47a
MnO_2 nanoflakes	0.5 M Na_2SO_4	CV (υ = 2 mV/s)	272.2	88.7% after 5000 cycles	47b
MnO_2/GPCN-SS	1 M Na_2SO_4	CP (*i* = 0.5 A/g)	438	/	48
MnO_2/graphene	1 M Na_2SO_4	CV (υ = 5 mV/s)	292.9	91.5% after 1000 cycles	49a
SG/CNTs/ MnO_2	1 M Na_2SO_4	CP (*i* = 0.5 A/g)	336.4	91.3% after 10000 cycles	49b
C1-0.04M-24h	0.5 M Na_2SO_4	CV (υ = 5 mV/s)	384.8	88.9% after 5000 cycles	this work

C2-0.04M-24h	0.5 M Na_2SO_4	CV (υ = 5 mV/s)	392.3	89.5% after 5000 cycles

Table S6. Rate capability of C1-*x*-*y* and C2-*x*-*y* electrodes

Samples	Rate capability (%)	Samples	Rate capability (%)
C1-0.01M-45min	55.1	C2-0.01M-45min	72.6
C1-0.04M-45min	69.4	C2-0.04M-45min	49.5
C1-0.10M-45min	60.2	C2-0.10M-45min	69.6
C1-0.01M-24h	66.8	C2-0.01M-24h	81.7
C1-0.04M-24h	68.5	C2-0.04M-24h	80.5
C1-0.10M-24h	51.3	C2-0.10M-24h	46.8

Table S7. The simulated resistance value for as-prepared electrodes

Samples	R_s	R_{ct}	Samples	R_s	R_{ct}
C1-0.01M-45min	3.35	9.41	C2-0.01M-45min	3.11	9.20
C1-0.04M-45min	3.70	5.92	C2-0.04M-45min	3.33	5.83
C1-0.10M-45min	4.38	11.50	C2-0.10M-45min	3.76	9.44
C1-0.01M-24h	2.07	6.26	C2-0.01M-24h	3.06	6.92
C1-0.04M-24h	1.97	5.93	C2-0.04M-24h	1.94	5.57
C1-0.10M-24h	3.87	22.75	C2-0.10M-24h	3.58	30.33