Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

For

Petal-like and cube-like manganese silicates derived from natural reed leaves for high-performance supercapacitors

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2.1 Material characterizations

X-ray diffraction (XRD) was used to identify the compositions and structures of the products using Bruker D8 Discover X-ray diffractometer with an ImS 2-D detection system (50 kV, 1000 mA). Raman spectra were recorded on a Renishaw InVia Raman microscope with a laser excitation sources of 532 nm. Fourier transform infrared spectroscopy (FTIR) spectra were collected on a Nicolet 6700 spectrometer from 4000 to 400 cm^{-1} using the KBr pellet technique. X-ray photoelectron spectrum (XPS) was taken on a Thermo ESCALAB 250XiX spectrometer with monochromatized Al Kα X-ray (hν = 1486.6 eV). Inductively Coupled Plasma (ICP, PerkinElmer, Optima 2000DV) was adopted to analyze the content of metal elements. A linear relationship was assumed between the edge position and oxidation state. The microstructures and chemical compositions of the products were characterized by a field-emission scanning electron microscope (FE-SEM, FEI Sirion) with an Energy-dispersive X-ray spectrometer (EDS) and transmission electron microscopy (JEOL-JEM2100F). The Brunauer-Emmet-Teller (BET) surface areas of the samples were determined by a Micromeritics ASAP-2020 porosity analyzer after being degassed at 150 ℃ for 10 h.

2.2 Electrochemical characterizations

The working electrodes were prepared by mixing active materials, carbon black and polyvinylidenedifluoride (PVDF) together in a weight of 8:1:1. Then a small quantity of N-methyl-2-pyrrolidone (NMP) was dropwise added into the mixture to dissolve it homogeneously. The mixed slurry was then coated onto a nickel foam with an area of 1×1 cm^2 and dried at 100 °C for 24 h to remove organic solvent, then pressed under a pressure of 10 MPa for 10 min to obtain the working electrode. The mass loading of active materials on the nickel foam was typically 3-4 mg cm^{-2}. Electrochemical characterization was carried out in a three-electrode system in 3 M KOH aqueous solution, where Hg/HgO and carbon rod were regarded as the reference electrode and the counter electrode, respectively. The flexible solid-state asymmetric supercapacitors (ASCs) were constructed from working electrode and activated carbon (AC) electrode using a membrane filter (NKK-PF30AC)

as a separator. The ASCs denoted as C-MnSi-0.5//AC and C-MnSi-2.0//AC. Both of the electrodes were prepared in the same way as that used for the preparation of the working electrode in the three-electrode system. For the purpose of getting a better performance of the device, the mass ratio of the positive to negative electrode is balanced on the basis of the equal charge between cathode and anode. The electrolyte was used 3 mol·L^{-1} polyvinyl alcohol/KOH (PVA/KOH) gel electrolyte. After dipping in the electrolyte, the entire device was sealed in plastic sheet to avoid the evaporation of electrolyte. The electrochemical characteristics of the ASCs devices were evaluated by galvanostatic charge-discharge (GCD), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements. The contribution of the nickel foam to the capacitance can be negligible [1]. The specific capacitance (C) of a single electrode was calculated on the basis of GCD according to the equation (1-2):

$$Cs = \frac{I \cdot \Delta t}{s \cdot \Delta V} \quad (1)$$

$$C = \frac{I \cdot \Delta t}{m \cdot \Delta V} \quad (2)$$

Where Cs (mF cm^{-2}) and C (F g^{-1}) represent areal and specific capacitance, respectively; I (A) denotes discharge current; Δt (s) signifies discharge time; s (cm^{-2}) corresponds to the area of working electrode; m (g) corresponds to the mass of the active material in the working electrode, and ΔV (V) refers to the potential window. The areal capacitance, areal capacity, energy density and power density of the ASC device were calculated on the basis of the equations (3-4):

$$E = \frac{1}{2} Cs \cdot (\Delta V)^2 \quad (3)$$

$$P = \frac{E}{\Delta t} \quad (4)$$

Where E (Wh·m^{-2}) is the energy density and P (W·m^{-2}) is the power density, respectively.

Figure S1

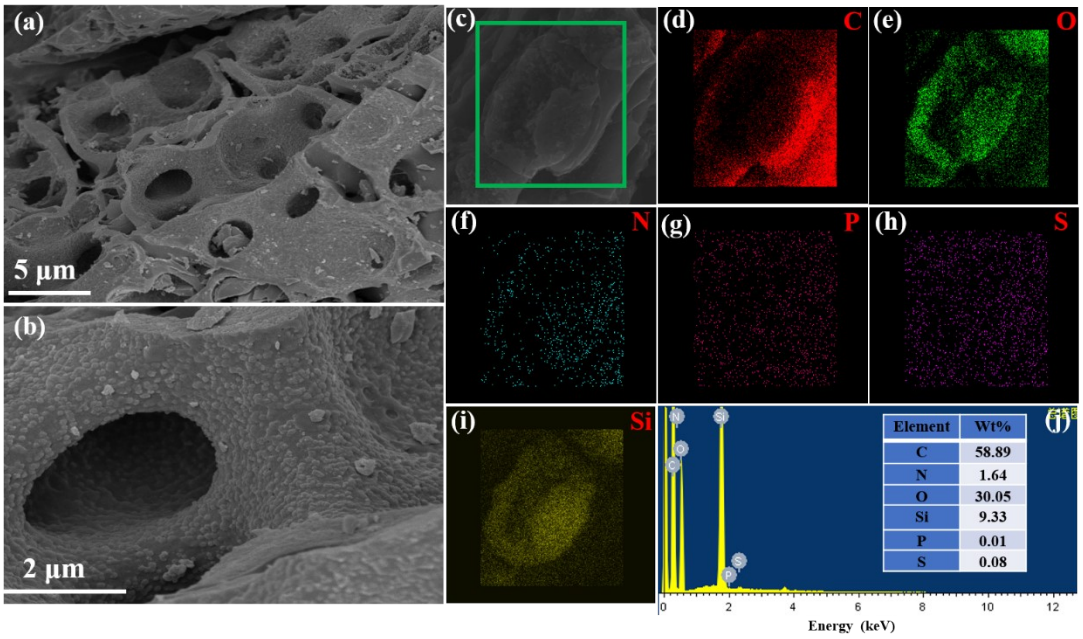

Fig. S1. FE-SEM and Elemental mapping images of C-SiO_2-N_2: (a-c) SEM image, (d) C-K, (e) O-K, (f) N-K, (g) P-K, (h) S-K, (i) Si-K, and (j) EDS of C-SiO_2-N_2.

Figure S2

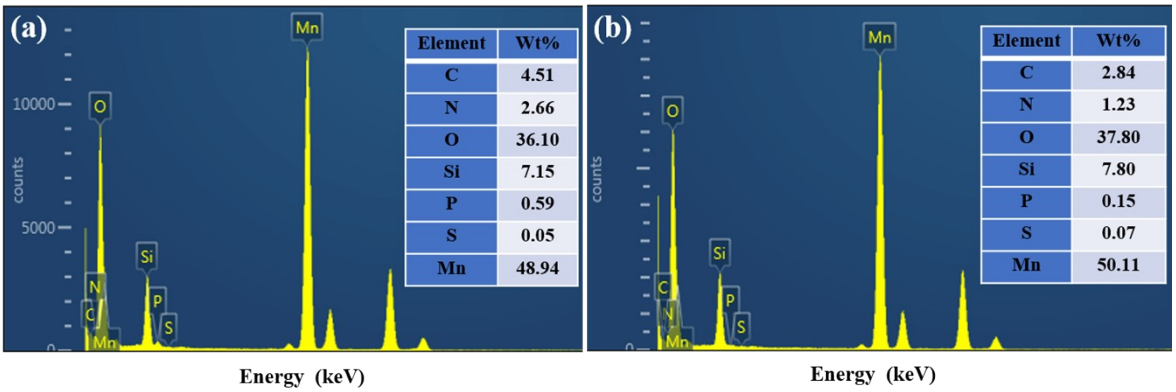

Fig. S2. EDS of C-MnSi-0.5 (a) and C-MnSi-2.0 (b).

Figure S3

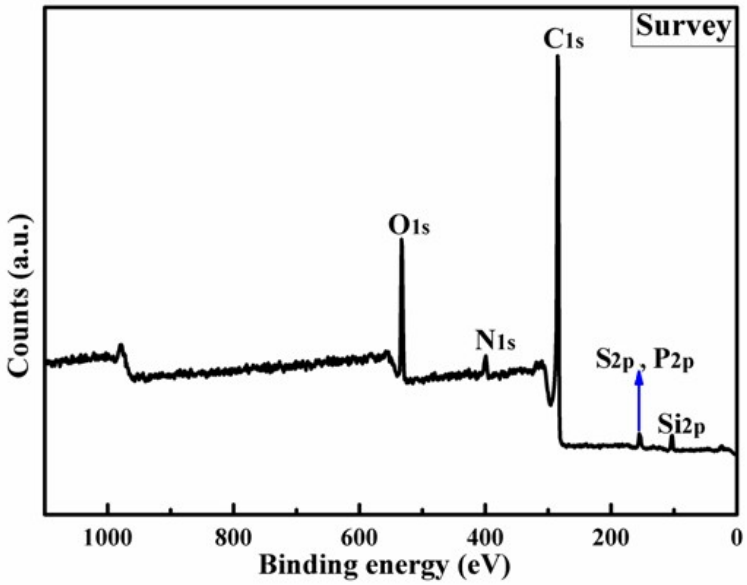

Fig. S3. Survey XPS spectrum of C-SiO_2-N_2.

Figure S4

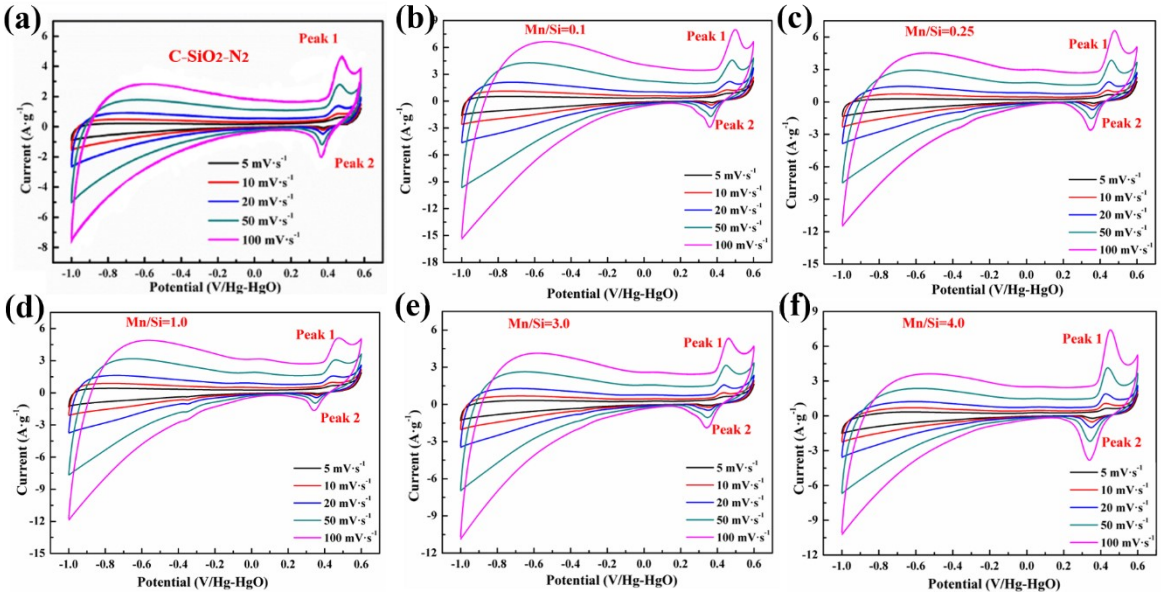

Fig. S4. CV curves of the C-SiO_2-N_2 (a), C-MnSi composites with various ratios of Mn/Si (0.1, 0.25, 1.0, 3.0 and 4.0) at different scan rates from 5 mV s^{-1} to 100 mV s^{-1} (b-f).

Figure S5

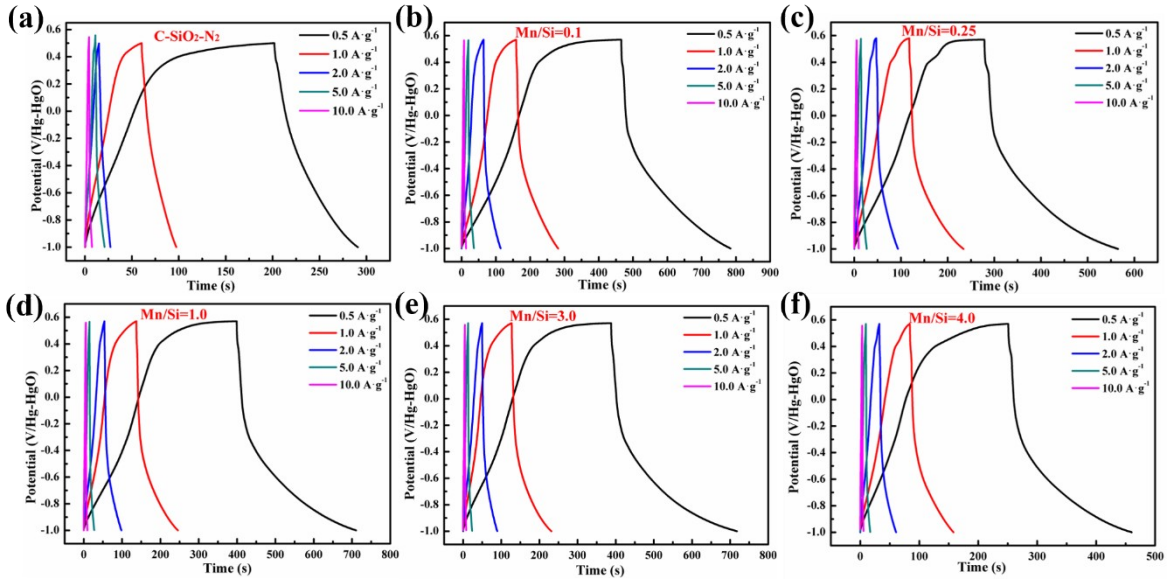

Fig. S5. GCD curves of the C-SiO_2-N_2 (a), C-MnSi composites with various ratios of Mn/Si (0.1, 0.25, 1.0, 3.0 and 4.0) at different current densities from 0.5 mA cm^{-2} to 10 mA cm^{-2} (b-f).

Figure S6

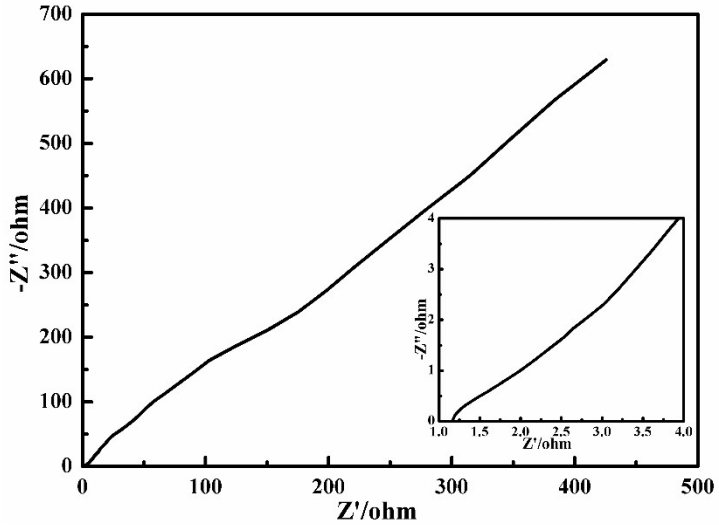

Fig. S6. Nyquist plot of C-SiO_2-N_2 in the frequency range from 100 kHz to 0.01 Hz.

Figure S7

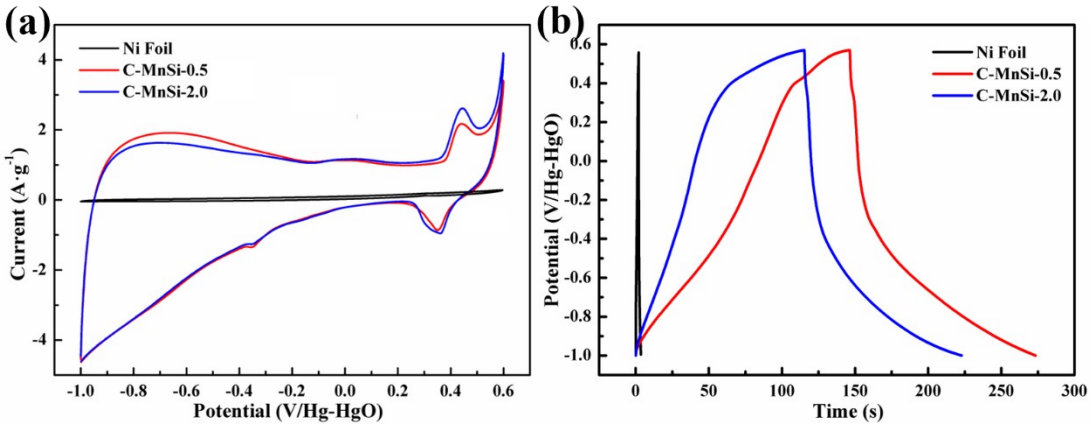

Fig. S7. (a) CV curves at scan rate of 20 mV·s^{-1} and (b) GCD curves at current density of 1 A·g^{-1} of Ni foil, C-MnSi-0.5 and C-MnSi-2.0.

Figure S8

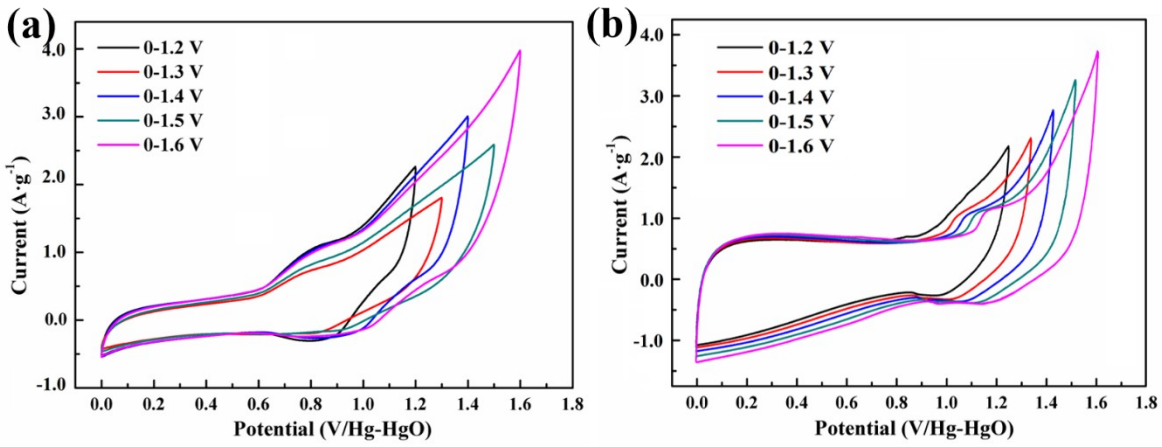

Fig. S8. CV curves of C-MnSi-0.5//AC (a) and C-MnSi-2.0//AC (b) supercapacitors at the scan of 20 mV s^{-1} on various potential limits.

Figure S9

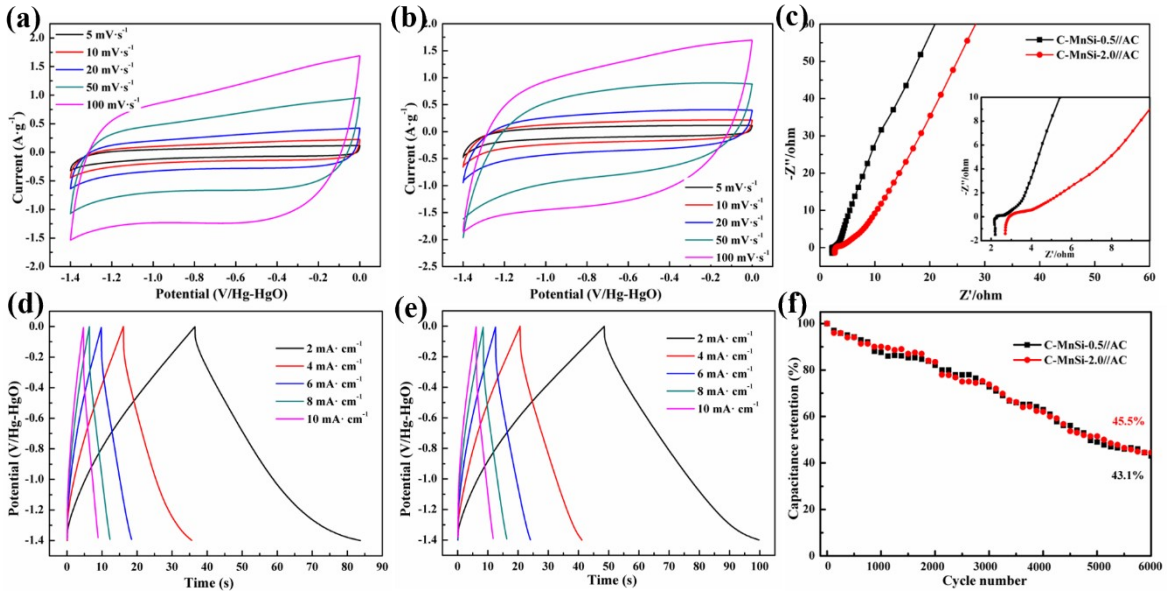

Fig. S9. Electrochemical performance of C-MnSi-0.5//AC and C-MnSi-2.0//AC ASC devices (on negative windows): (a) and (b) CV curves at different scan rates; (d) and (e) GCD curves at different current densities; (c) Nyquist plots in the frequency ranging from 100 kHz to 0.01 Hz; (f) Cycling performance.

Figure S10

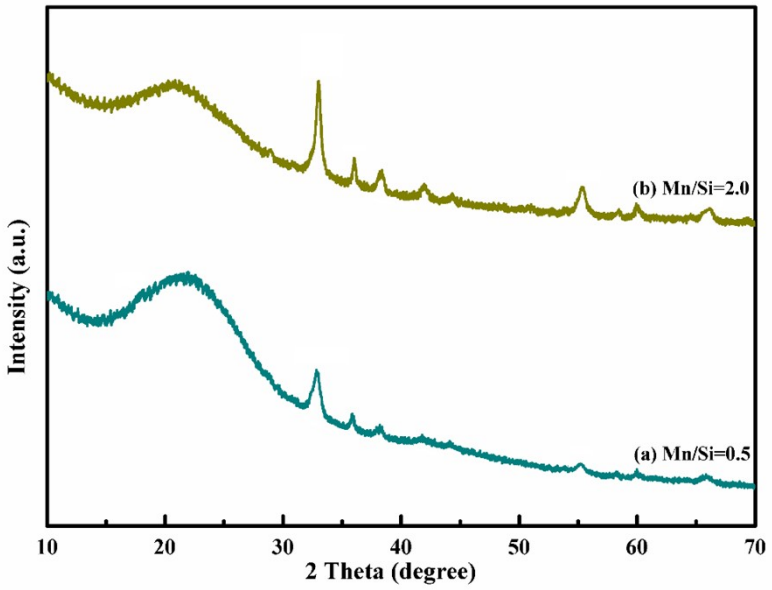

Fig. S10. The XRD patterns of the C-MnSi-0.5 (a) and C-MnSi-2.0 (b) electrodes after cycling.

Figure S11

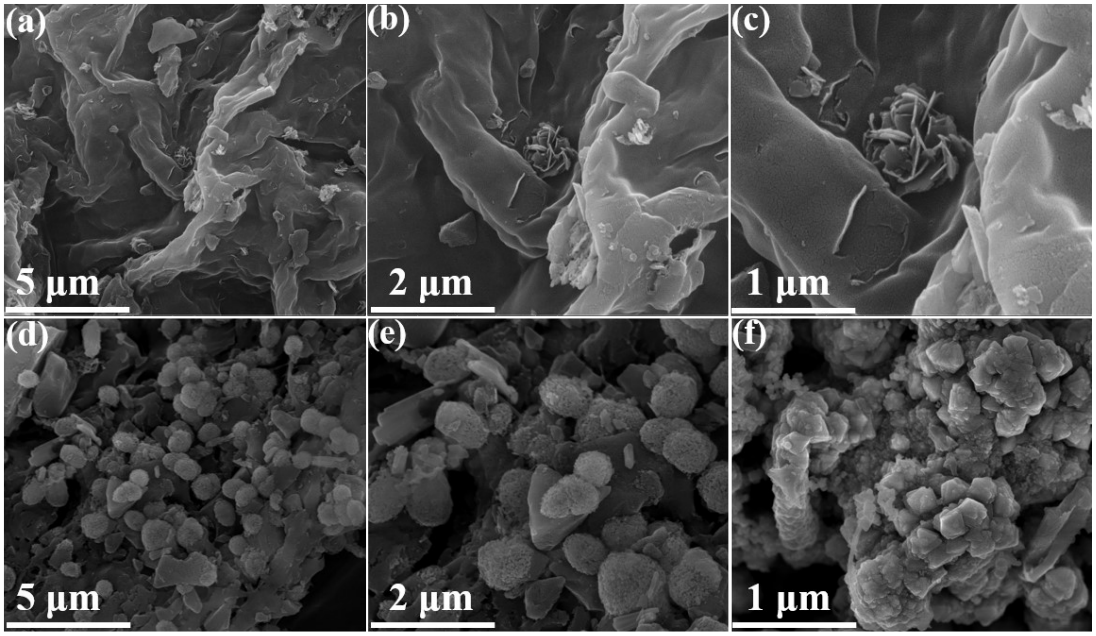

Fig. S11. The SEM images of the C-MnSi-0.5 (a-c) and C-MnSi-2.0 (d-f) electrodes after cycling.

Figure S12

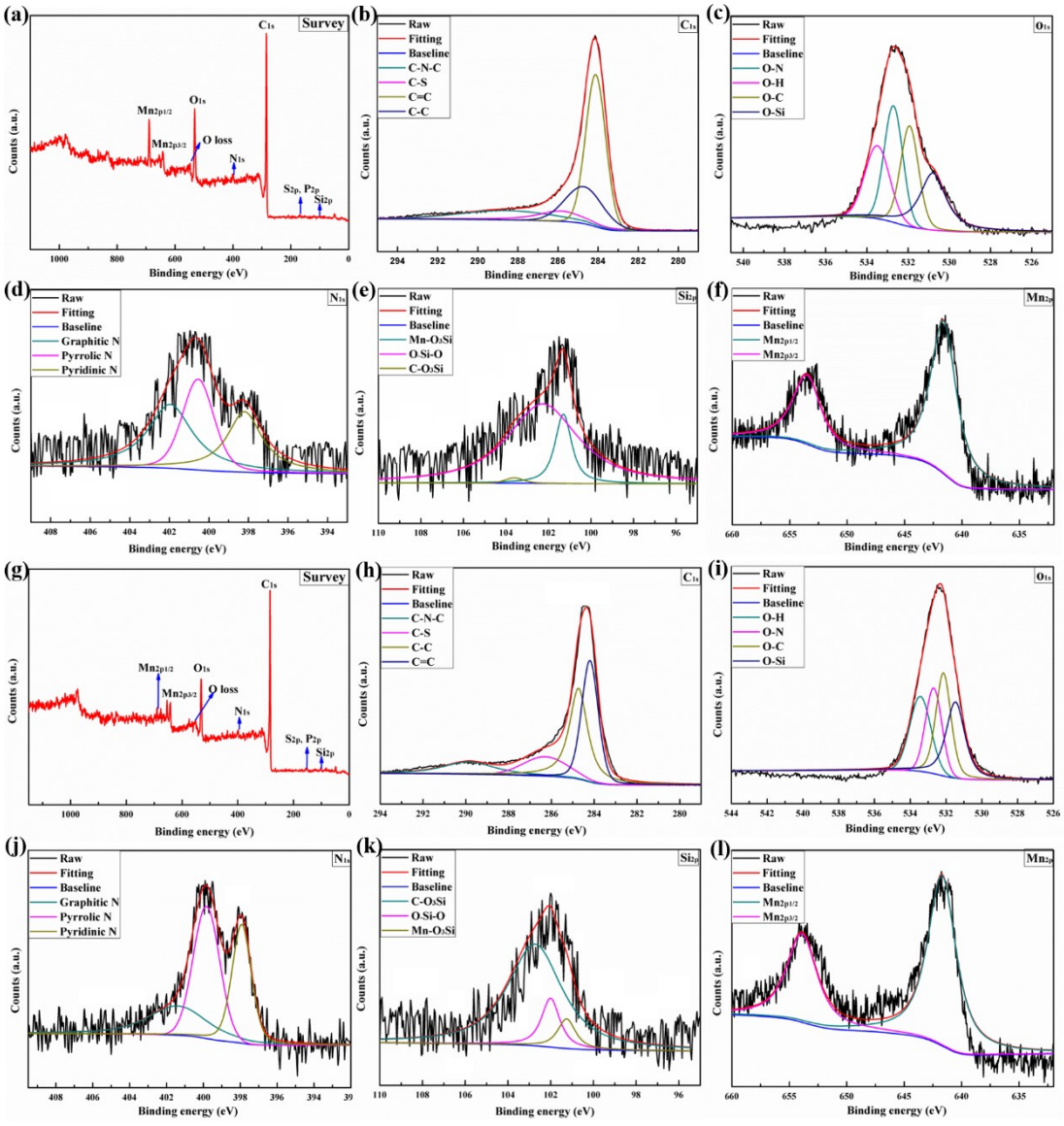

Fig. S12. XPS spectra of C-MnSi-0.5 (a-f) and C-MnSi-2.0 (g-l) electrodes after cycling: (a, g) Survey XPS spectrum; (b-f, h-l) Core-level spectra of C_{1s}, O_{1s}, N_{1s}, Si_{2p} and Mn_{2p}, respectively.

Table S1. Pore Parameters of C-SiO_2-N_2, C-MnSi-0.5 and C-MnSi-2.0.

sample	BET surface area (m^2 g^{-1})	total pore vol (cm^3 g^{-1})
C-SiO_2-N_2	418	0.389
C-MnSi-0.5	554	0.543
C-MnSi-2.0	577	0.561

Table S2. Comparison of the specific capacitance of the N, P, S-doped C-$(Mn_2O_3)_3MnSiO_3$ and the previously reported Si- and Mn-based materials.

Si- or Zn-based materials	Electrolyte [a]	Potential /V	Capacitance/mF cm^{-2}	Cycling capability	Reference
$Ni_3Si_2O_5(OH)_4$/RGO	2 M KOH	0.2 ~ 0.6	178.9 F g^{-1}, 1 A g^{-1}	97.6 % after 5000	[2]
$MnSiO_3$	6 M KOH	0.2~0.6	251 F·g^{-1}, 0.6 A·g^{-1}	—	[3]
Manganese silicate drapes	1 M KOH	-0.5 ~ 0.4	283 F g^{-1}, 0.5 A g^{-1}	74.7 % after 1000	[4]
$(Ni, Co)_3Si_2O_5(OH)_4$	1 M KOH	0 ~ 0.5	144 F g^{-1}, 1 A g^{-1}	99.3 % after 10000	[5]
Mesoporous-Li_2MnSiO_4	2 M KOH	0 ~ 0.55	120 F g^{-1}, 20 mV·s^{-1}	85.7 % after 500	[6]
$Ni_3Si_2O_5(OH)_4$	3 M KOH	0 ~ 0.5	132.4 F g^{-1}, 0.5 A g^{-1}	100 % after 10000	[7]
$Co_3(Si_2O_5)_2(OH)_2$	6 M KOH	0.1 ~ 0.55	237 F g^{-1}, 5.7 mA cm^{-2}	95 % after 150	[8]
$Co_3Si_2O_5(OH)_4$	6 M KOH	0 ~ 0.5	570 F g^{-1}, 0.7 A g^{-1}	—	[9]
$MnSiO_3$/GO	1 M Na_2SO_4	-0.2 ~ 1	262.5 F g^{-1}, 0.5 A g^{-1}	53 % after 5000	[10]
$Co_xNi_{3-x}Si_2O_5(OH)_4$	3 M KOH	-0.80 ~ 0.6	226 F g^{-1}, 0.5 A g^{-1}	99 % after 10000	[11]
MnO_2/carbon cloth	0.1 M Na_2SO_4	0 ~ 0.8	230 mF cm^{-2}, 10 mV s^{-1}	98.5 % after 3000	[12]
CoSi hollow sphere	3 M KOH	0 ~ 0.5	452.8 F g^{-1}, 0.5 A g^{-1}	89 % after 10000	[13]
SWCNT/cellulose/PANI	1 M H_2SO_4	-0.2 ~ 0.6	330 mF cm^{-2}, 0.2 mA cm^{-2}	79% after 1000	[14]
$Zn_4Si_2O_7(OH)_2·H_2O$	3 M KOH	-1.0 ~ 0.6	341 mF cm^{-2}, 5 mV·s^{-1}	99 % after 10000	[15]
$Co_2Si_2O_4$	6 M KOH	0 ~ 0.5	267 mF cm^{-2}, 5 mV·s^{-1}	90 % after 10000	[16]
C-MnSi-0.5	**3 M KOH**	**-1.0 ~ 0.6**	**376 F g^{-1}, 0.5 A g^{-1}**	**99 % after 10000**	**This work**
C-MnSi-2.0	**3 M KOH**	**-1.0 ~ 0.6**	**491 F g^{-1}, 0.5 A g^{-1}**	**99 % after 10000**	**This work**

a M = mol L^{-1}

References

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