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Supporting Information

Nano-embedded microstructured FeS_2@C as a high capacity and cycle-stable Na-storage anode with the optimized ether-based electrolyte

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1. X-ray photoelectron spectra of the FeS_2@C

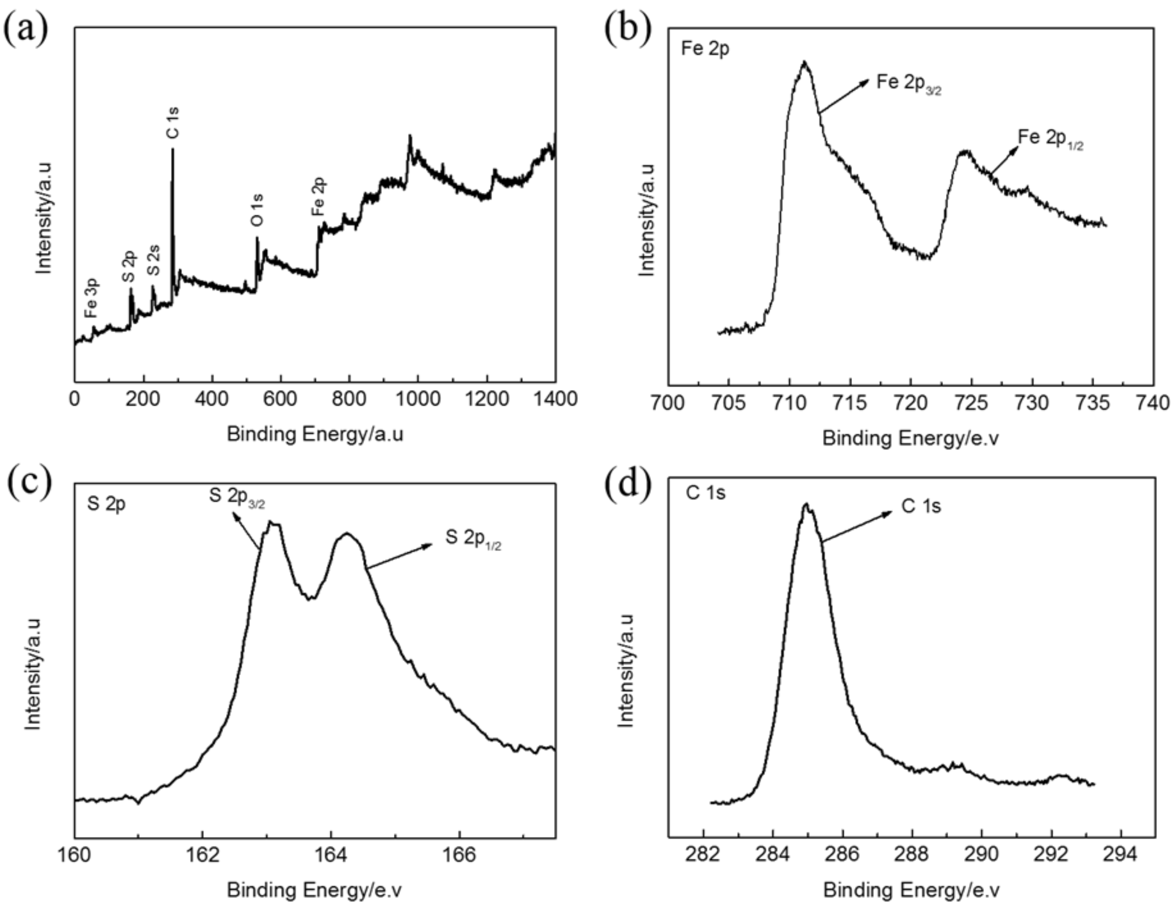


Fig. S1. Typical XPS spectra of the FeS_2@C composite: (a) survey spectra, (b) high-resolution image of Fe 2p band, (c) high-resolution image of S 2p band, (d) high-resolution image of C 1s band

2. Thermogravimetric (TG) analysis of the FeS_2@C

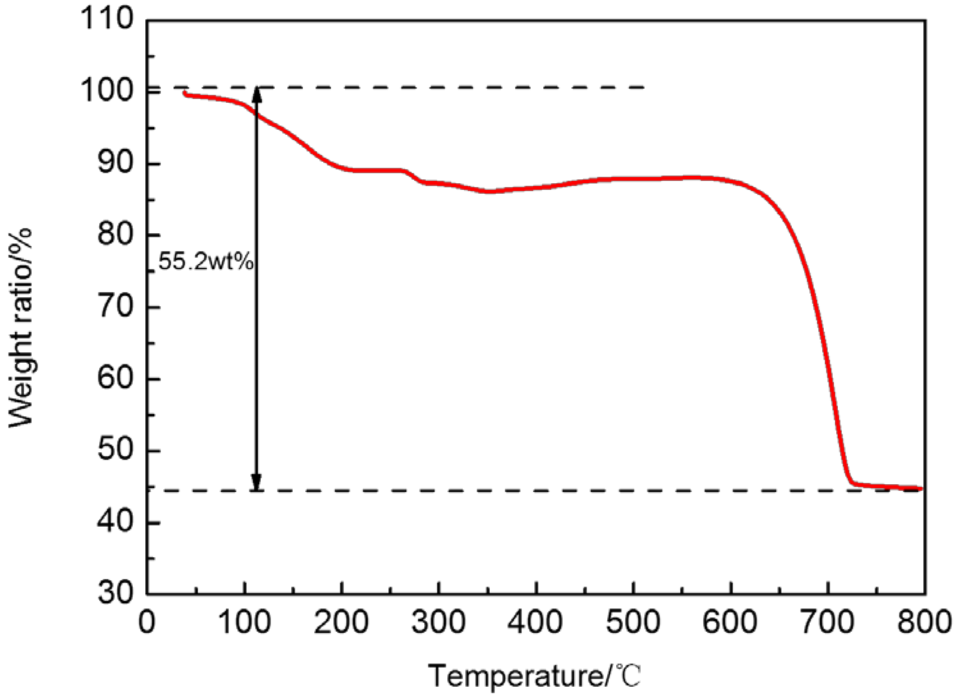


Fig. S2. TG curves of the FeS_2@C composite

Under the air atmosphere, the FeS_2@C experience the transformation of FeS_2 to Fe_2O_3 and the oxidation of C. Taking into acount of the weight loss of the former tranfermation, the contents of carbon is calculated to be 32.4%.

3. SEM images of the as-prepared FeS_2@C

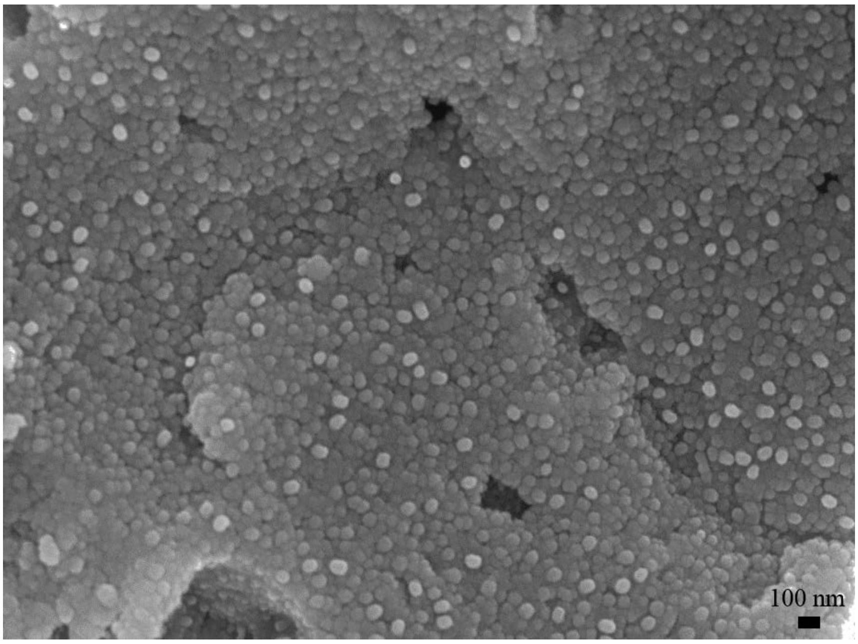


Fig. S3. SEM image of the as prepared FeS_2@C

4. N_2 adsorption–desorption isotherm of the as-prepared FeS_2@C

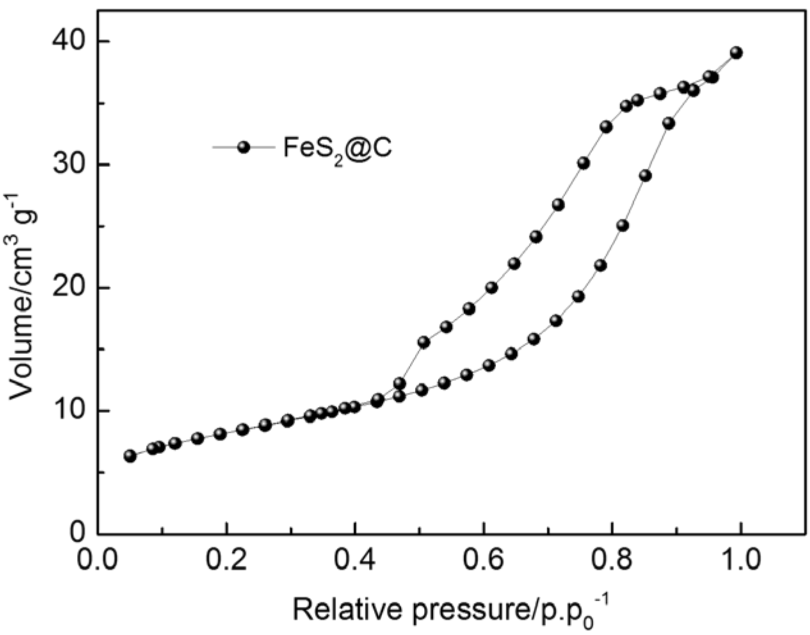


Fig. S4. N_2 adsorption–desorption isotherm of the as prepared FeS_2@C

5. **Cyclic voltammetry analysis of the FeS_2@C in different ether- and ester-based electrolyte**

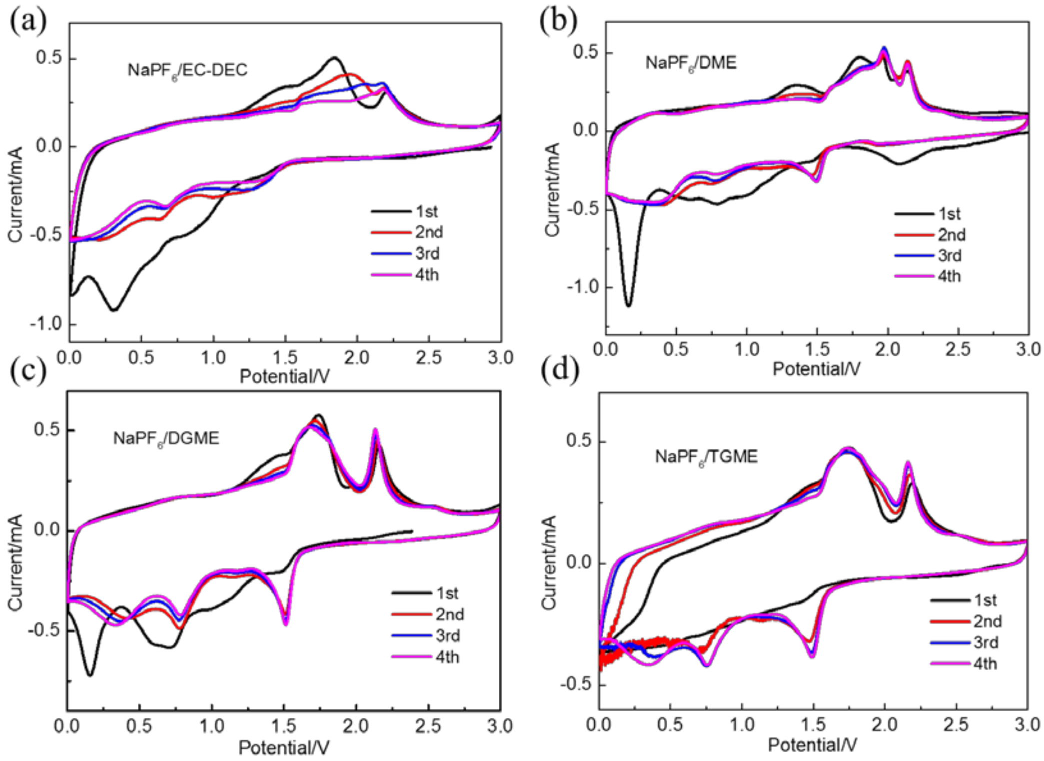


Fig. S5. CV curves of the as-prepared FeS_2@C electrode in (a) $NaPF_6$/EC-DEC; (b) $NaPF_6$/DME; (c) $NaPF_6$/DGME; (d) $NaPF_6$/TGME. Scanning rates: 0.2 mV s^{-1}; voltage range: 0.005 - 3 V

6. Cycling performances of the FeS_2@C in the electrolytes with different solvents

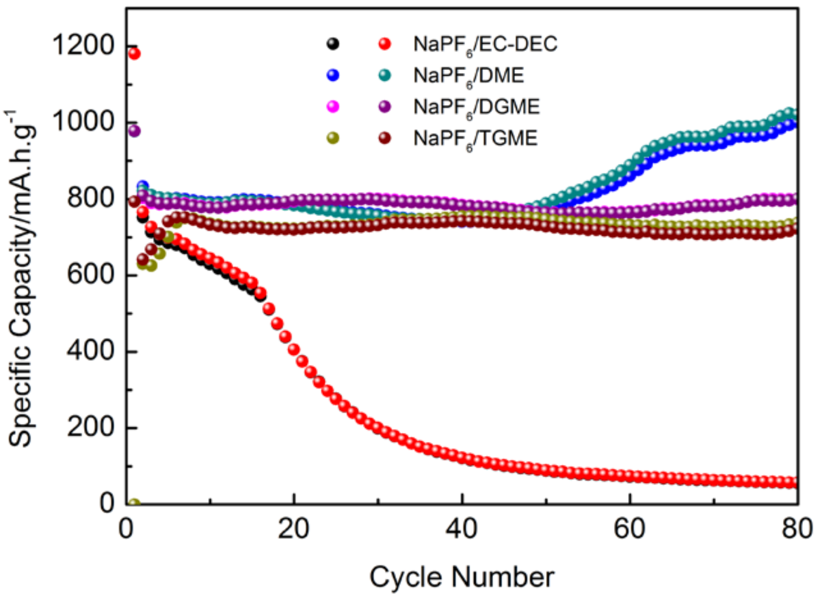
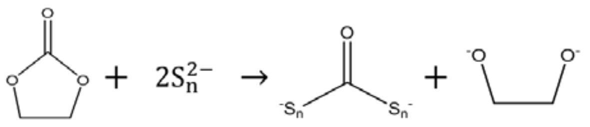


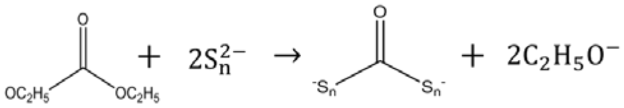
Fig. S6. Cycling performances of the FeS_2@C at 0.5 A g^{-1} in the electrolytes with different solvents: $NaPF_6$/EC-DEC, $NaPF_6$/DME, $NaPF_6$/DGME, $NaPF_6$/TGME. Voltage range: 0.005 ~ 3V

7. The side reactions between carbonate solvents and polysulfide



EC

Equation S 1



DEC

Equation S 2

8. The Na storage performances of carbon in the electrolyte of $NaPF_6$/DME.

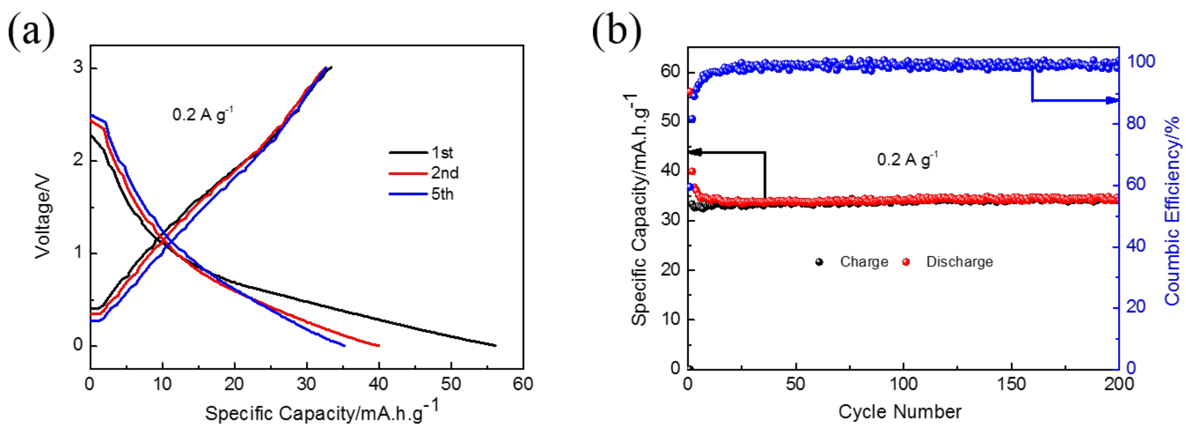


Fig. S7. (a)The charge-discharge profiles and (b) cycling performances of carbon derived from critic acid at 0.2 A g^{-1};

The carbon derived from critic acid can deliver a reversible capacity of 32 mAh g^{-1}, respectively. As the carbon contents in the FeS_2@C composite is 32.4%, the capacities contribution from carbon is 15 mAh g^{-1}.

9. Electrochemical impedance spectra (EIS) analysis of the FeS_2@C at the charged state after the 1st and 30 th cycle in the electrolytes with different solvents and Na salts

Table S1 Fitting results of the Nyquist plots of the FeS_2 electrode cycled in the electrolytes with different solvents

Cycle	Samples	R_S(Ω)	R_{SEI} (Ω)	CPE_S(F)	R_{ct}(Ω)	CPE_{dl}(F)	Chi-Squared
1 st	B_{EC-DEC}	7.5	25.0	2.2×10^{-5}	14.8	2.0×10^{-5}	3.8×10^{-3}
	B_{DME}	5.7	1.3	4.3×10^{-7}	2.3	1.1×10^{-4}	2.5×10^{-3}
	B_{DGME}	9.0	7.3	3.4×10^{-7}	9.2	8.8×10^{-4}	1.5×10^{-3}
	B_{TGME}	21.8	14.5	6.5×10^{-6}	34.8	1.1×10^{-4}	6.6×10^{-4}
30 th	B_{EC-DEC}	9.6	41.7	1.9×10^{-5}	346.4	2.6×10^{-5}	2.5×10^{-4}
	B_{DME}	5.0	0.6	1.6×10^{-6}	1.7	1.8×10^{-4}	3.0×10^{-3}
	B_{DGME}	17.5	6.5	7.8×10^{-7}	8.7	2.2×10^{-4}	3.5×10^{-4}
	B_{TGME}	8.4	13.7	1.0×10^{-4}	32.6	2.8×10^{-5}	7.8×10^{-5}

Table S2 Fitting results of the Nyquist plots of the FeS_2 electrode cycled in the electrolytes with different Na salts

Cycle	Samples	R_S(Ω)	R_{SEI} (Ω)	CPE_S(F)	R_{ct}(Ω)	CPE_{dl}(F)	Chi-Squared
1st	B_{NaClO4}	19.1	207.7	9.5×10^{-5}	66.8	1.8×10^{-4}	1.6×10^{-3}
	$B_{NaCF3SO3}$	50.4	5.7	6.9×10^{-6}	42.1	3.2×10^{-4}	1.2×10^{-3}
	B_{NaPF6}	5.7	1.3	4.3×10^{-7}	2.3	1.1×10^{-4}	2.5×10^{-3}
30th	B_{NaClO4}	2.2	340.8	3.3×10^{-4}	297.0	2.0×10^{-5}	3.0×10^{-4}
	$B_{NaCF3SO3}$	65.4	20.5	2.1×10^{-5}	181.2	1.9×10^{-5}	3.9×10^{-4}
	B_{NaPF6}	5.0	0.6	1.6×10^{-6}	1.7	1.8×10^{-4}	3.0×10^{-3}

10. Cyclic voltammetry analysis of the FeS_2@C in DME-based electrolyte with different Na salts

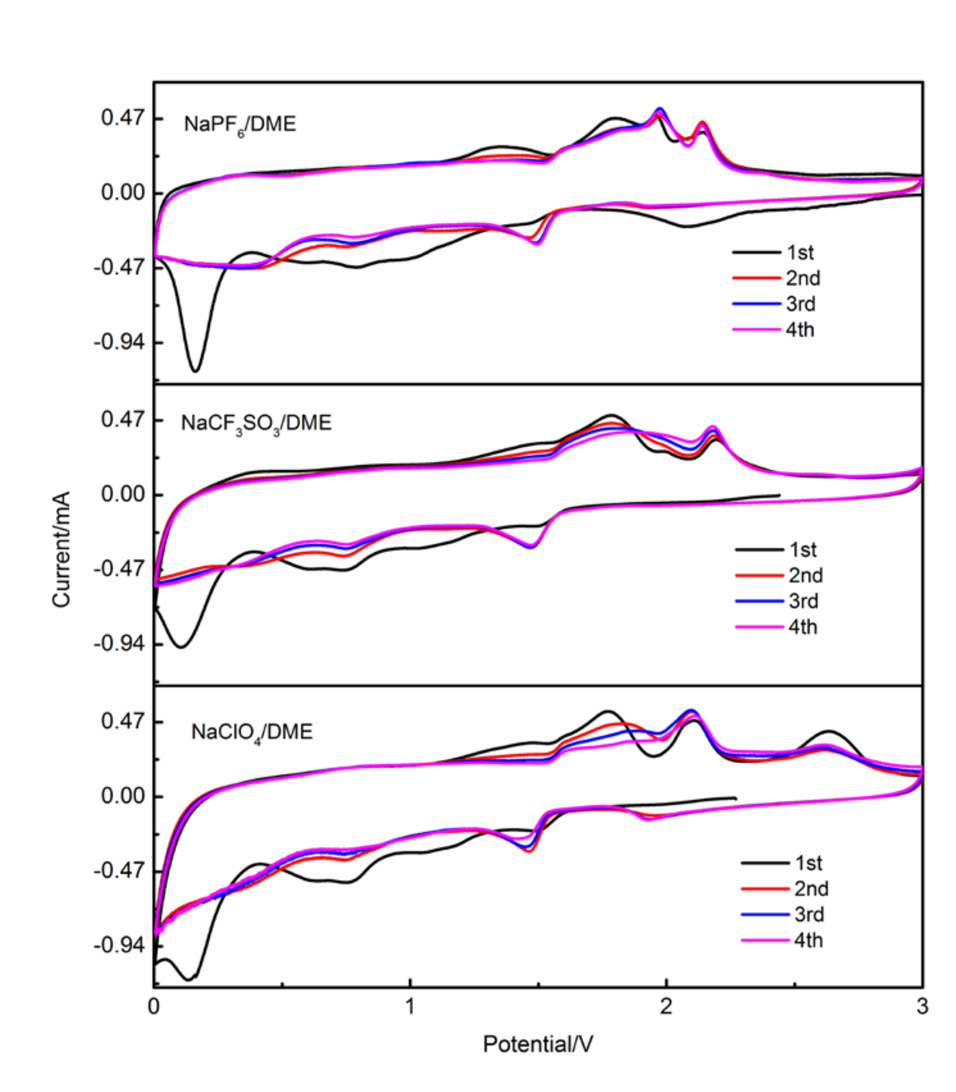


Fig. S8. CV curves of the as-prepared FeS_2@C electrode in DME-based electrolyte with different Na salts: $NaPF_6$/DME, $NaCF_3SO_3$/DME, $NaClO_4$/DME. Scanning rates: 0.2 mV s^{-1}; voltage range: 0.005 - 3 V.

As shown in Fig. S8, in the CV curves of the electrode tested in $NaClO_4$/DME, there are obvious redox peaks located at 2.0/2.5 V, which cannot be observed in the CV curves of that in $NaSO_3CF_3$/DME and $NaPF_6$/DME. As the S/Fe mole ratios of the electrode obtained in $NaClO_4$/DME (1.06) is much lower than that of the pristine electrode, this peak can be ascribed to the redox reactions of the polysulfide which are dissolved in the electrolyte. While in in $NaSO_3CF_3$/DME and $NaPF_6$/DME, the S/Fe mole ratios of the electrode is 1.39 and 1.95, so that the redox peaks located at 2.0/2.5 V are insignificant.

11. XPS characterizations on the surface of the FeS_2@C electrode obtained in in DME-based electrolyte with different Na salts

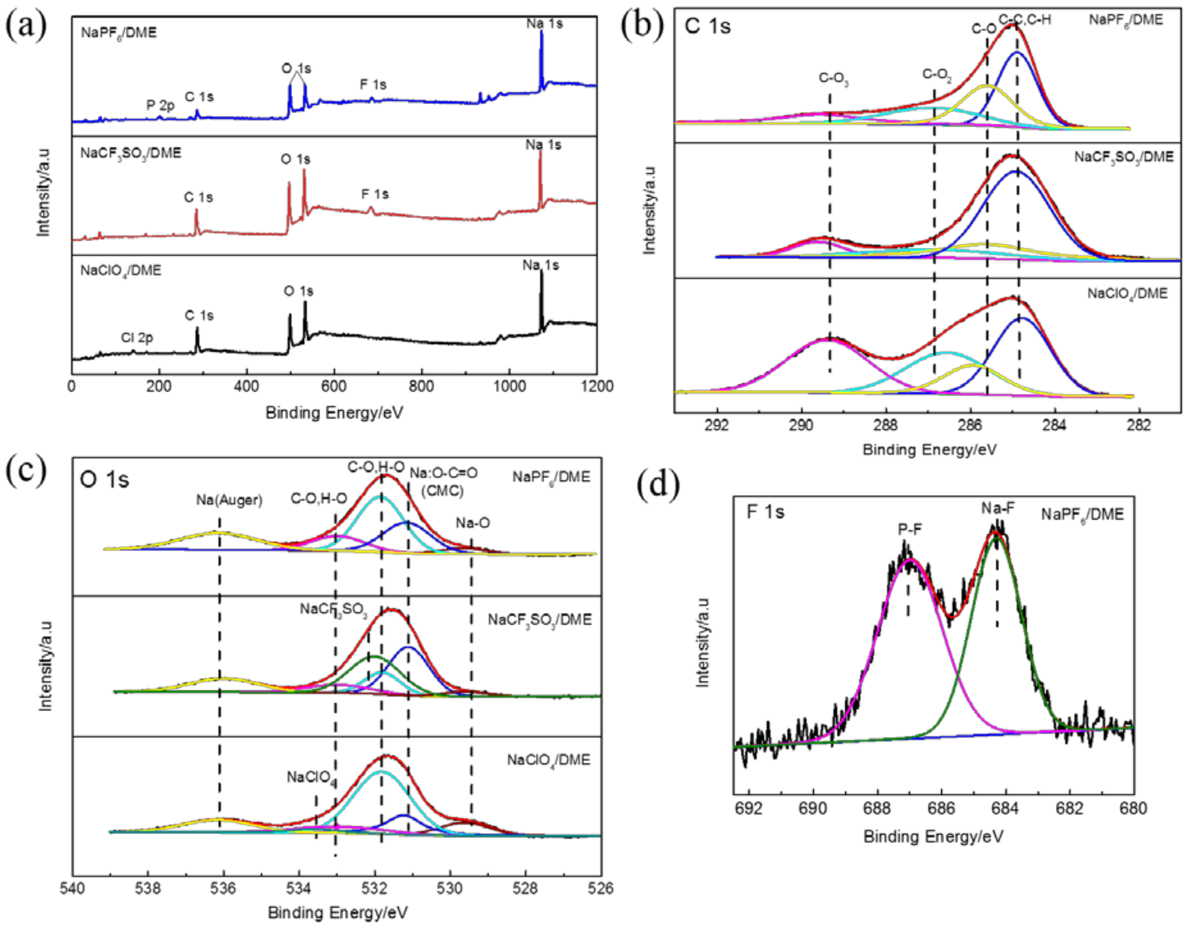


Fig. S9. Typical XPS spectra of the electrode cycled in $NaPF_6$/DME, $NaCF_3SO_3$/DME and $NaClO_4$/DME after the initial discharge process: (a) survey spectra, (b) high-resolution image of C 1s band, (c) high-resolution image of O 1s band, (d) high-resolution image of F 1s band.

As shown in the XPS spectra, the compounds in the SEI films formed in $NaPF_6$/DME are mainly NaF, Na_2CO_3, Na_2O, RCH_2ONa, phosphates, et al. The SEI films formed in $NaCF_3SO_3$/DME are mainly composed of NaF, Na_2CO_3, Na_2O, RCH_2ONa, whereas those formed in the $NaClO_4$/DME are composed of Na_2CO_3, Na_2O, RCH_2ONa and chlorates. It is noteworthy that the SEI films formed in $NaPF_6$/DME show an increase in the NaF contents and decrease in the Na_2CO_3 contents compared to that of $NaCF_3SO_3$/DME and $NaClO_4$/DME.

12. Elemental contents of the electrodes analysis of the FeS_2@C in DME-based electrolyte with different Na salts

Table S3 Elemental contents of the FeS_2@C electrodes cycled in the DME-based electrolyte with $NaClO_4$, $NaCF_3SO_3$ and $NaPF_6$ after 30 cycles using XPS tester

Sample	Na(mol%)	F(mol%)	O(mol%)	C(mol%)	P(mol%)	Fe(mol%)	S(mol%)	S/Fe ratios
B_{NaClO4}	5.69	0.54	18.35	72.72	0.37	1.15	1.22	1.06
$B_{NaCF3SO3}$	6.19	0.74	18.68	69.11	0.4	2.06	2.86	1.39
B_{NaPF6}	5.87	0.49	14.88	73.44	0.42	1.68	3.27	1.95

13. The Na storage performances of the FeS_2@C in various ether-based electrolytes (DME, DGME, TGME) with different Na salts ($NaPF_6$, $NaCF_3SO_3$, NaFSI, NaTFSI, $NaClO_4$)

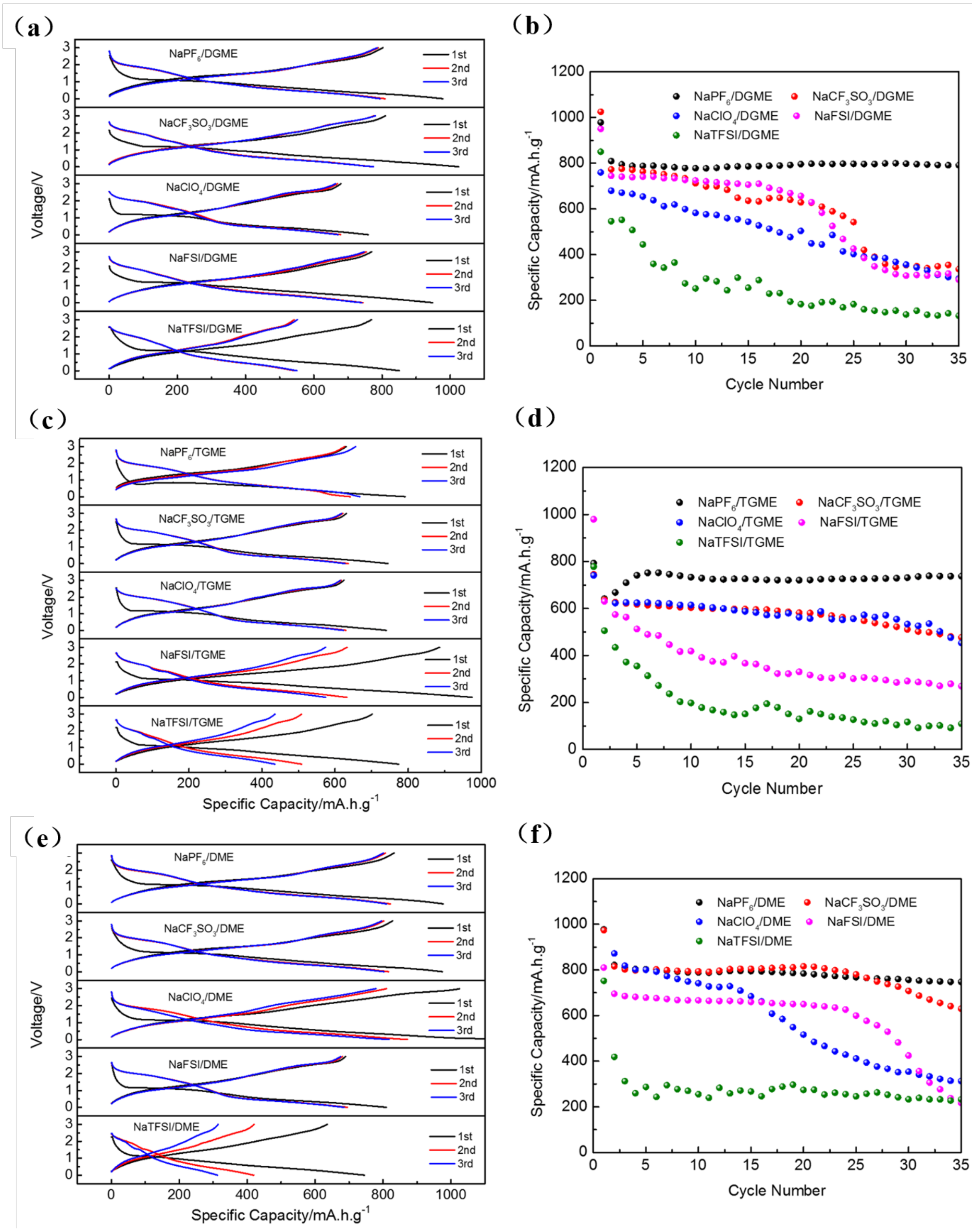


Fig. S10. Charge-discharge profiles of the FeS_2@C in DGME-based (a), TGME-based (c) and DME-based (e) electrolytes in the voltage range of 0.005~3 V; Comparison of the cycling performances of FeS_2@C in in DGME-based (b), TGME-based (d) and DME-based (f) electrolytes. Current density: 500 mA g^{-1}.

14. Comparison of the Na storage performances in different electrolyte systems.

Table S4 Comparison of the Na storage performances of the FeS_2@C electrodes in different electrolyte systems.

Electrolyte	Initial discharge/charge capacity(mAh g^{-1})	Initial coulombic efficiency(%)	Coulombic efficiency during cycling(%)	Capacity retention after 30 cycles(%)
$NaPF_6$/EC+DEC	1180.8/752.1	63.7	93.9	27.9
$NaPF_6$/DME	977.8/832.5	85.1	99.9	95.0
$NaPF_6$/DGME	978.6/802.9	82.0	99.8	98.6
$NaPF_6$/TGME	793.2/630.7	79.5	99.8	100
$NaClO_4$/DME	1257.3/1025.2	81.5	95.2	41.4
$NaClO_4$/DGME	759.2/679.6	89.5	98.3	52.3
$NaClO_4$/TGME	740.6/624.5	84.3	99.3	72
$NaCF_3SO_3$/DME	974/827.9	85.0	97.6	86.1
$NaCF_3SO_3$/DGME	1025.3/810.2	79.0	99.5	45.6
$NaCF_3SO_3$/TGME	745.0/631.2	84.7	99.4	74.9
NaFSI/DME	809.6/689.7	85.2	98.7	62
NaFSI/DGME	950.0/770.3	81.1	99.2	41.2
NaFSI/TGME	975.7/886.2	90.8	99.6	46.2
NaTFSI/DME	745.3/636.1	85.4	99.0	31
NaTFSI/DGME	851/769.1	90.4	99.4	25.3
NaTFSI/TGME	774.2/702.2	90.7	99.2	23.1

15. Ionic conductivity of different electrolytes

Table S5 Ionic conductivity of different electrolytes with different solvents and Na salts

Sample	Ionic conductivity (μs cm^{-1})
1M $NaPF_6$/DME	12890
1M $NaPF_6$/DGME	7320
1M $NaPF_6$/TGME	2580
1M $NaPF_6$/EC-DEC	8920
1M $NaCF_3SO_3$/DME	2120
1M $NaClO_4$/DME	1120

As shown in Table S4, 1M $NaPF_6$/DME demonstrate the highest ionic conductivity of 12890 μs cm^{-1}.

16. Na storage performances of the FeS_2@C in $NaPF_6$/DME.

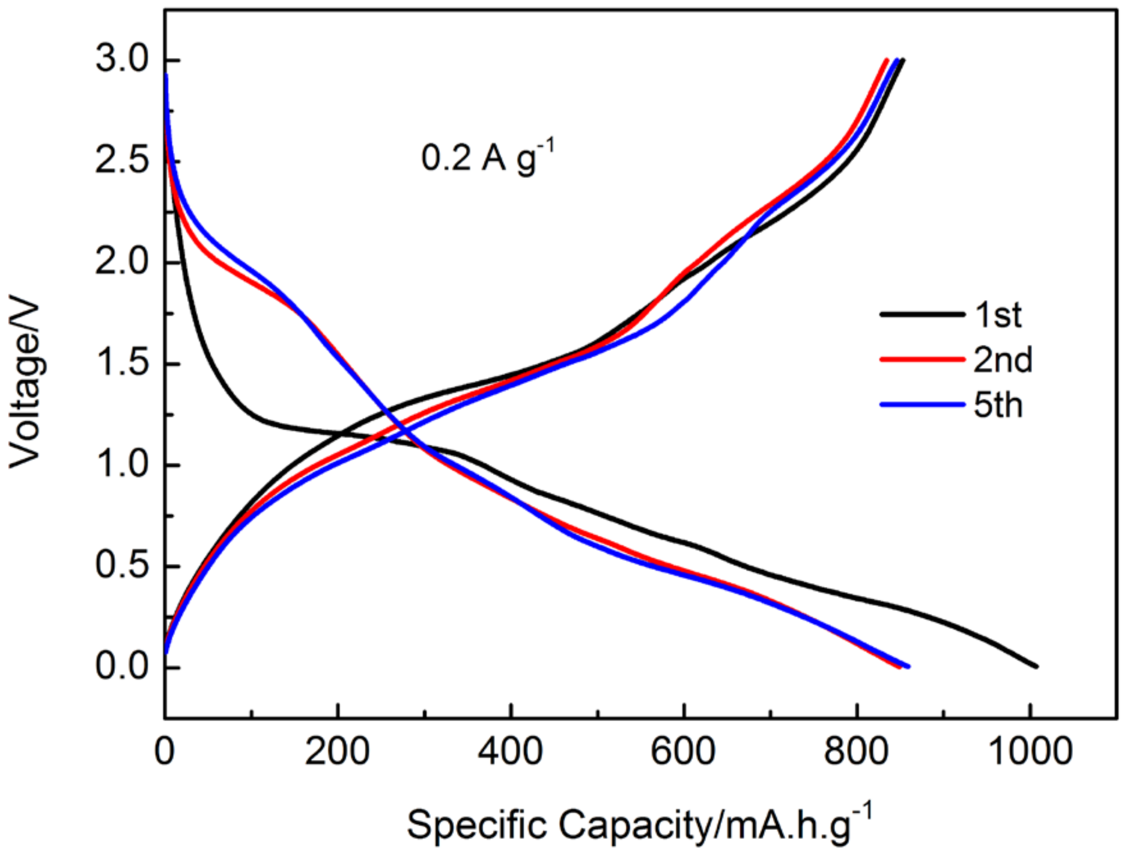


Fig. S11 Charge-discharge profiles of the FeS_2@C in $NaPF_6$/DME at 0.2 A g^{-1}. Voltage range: 0.005 ~ 3 V.

At the current density of 0.2 A g^{-1}, the FeS_2@C deliver an initial charge/discharge capacity of 1007.5 /853 mAh g^{-1}, corresponding to the initial coulombic efficiency of 84.7%.

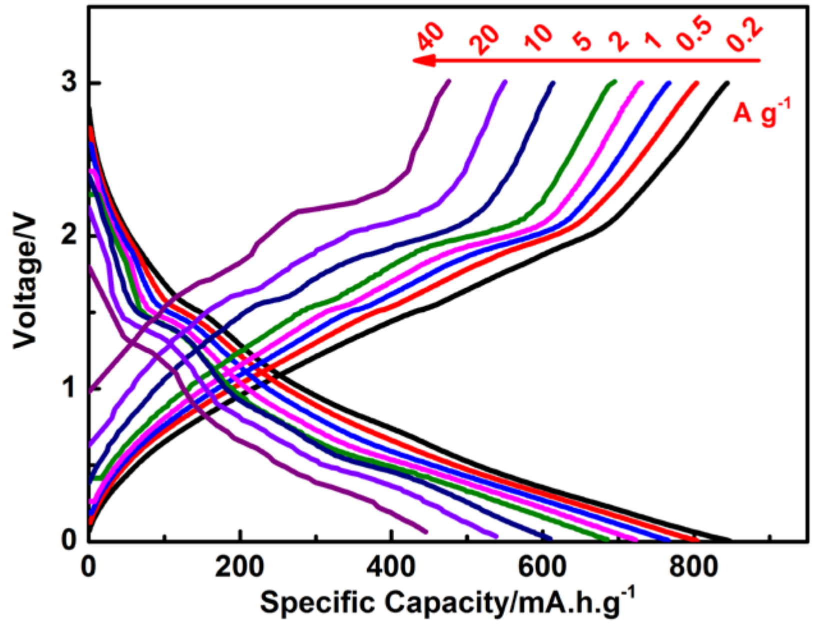


Fig. S12 Charge-discharge profiles of the FeS_2@C in $NaPF_6$/DME at different current densities from 0.2 to 40 A g^{-1}. Voltage range: 0.005 ~ 3 V.

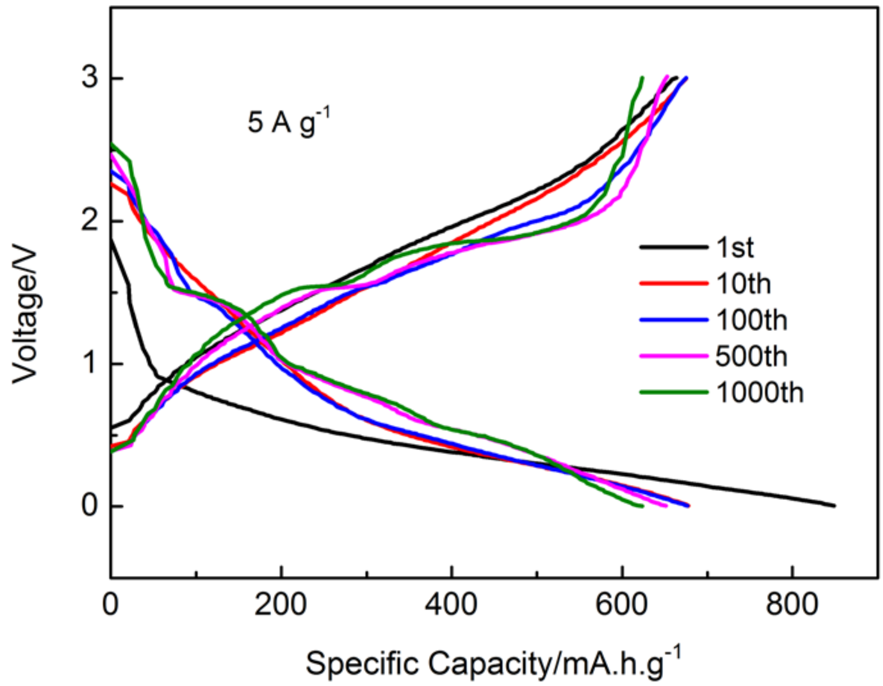


Fig. S13 Charge-discharge profiles of the FeS_2@C in $NaPF_6$/DME at 5 A g^{-1} of different cycles. Voltage range: 0.005 ~ 3 V.

17. Na storage performances of the FeS_2 without carbon.

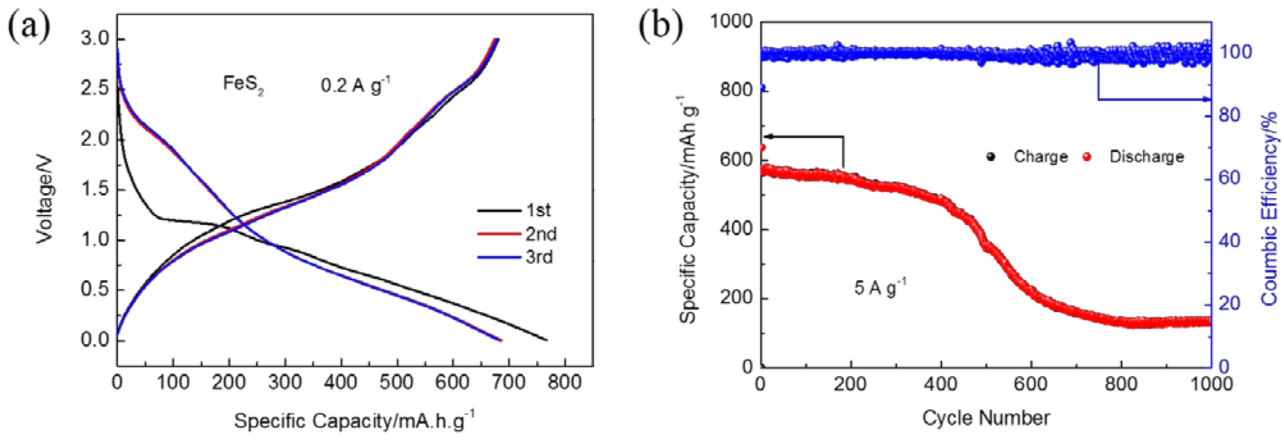


Fig. S14 (a) Charge-discharge profiles of the FeS_2 in $NaPF_6$/DME at 0.2 A g^{-1}; (b) cycling performances of FeS_2 at 5 A g^{-1}: voltage range: 0.005 ~ 3 V.

18. SEM and TEM images of FeS_2@C electrode after different cycles at the fully charged state.

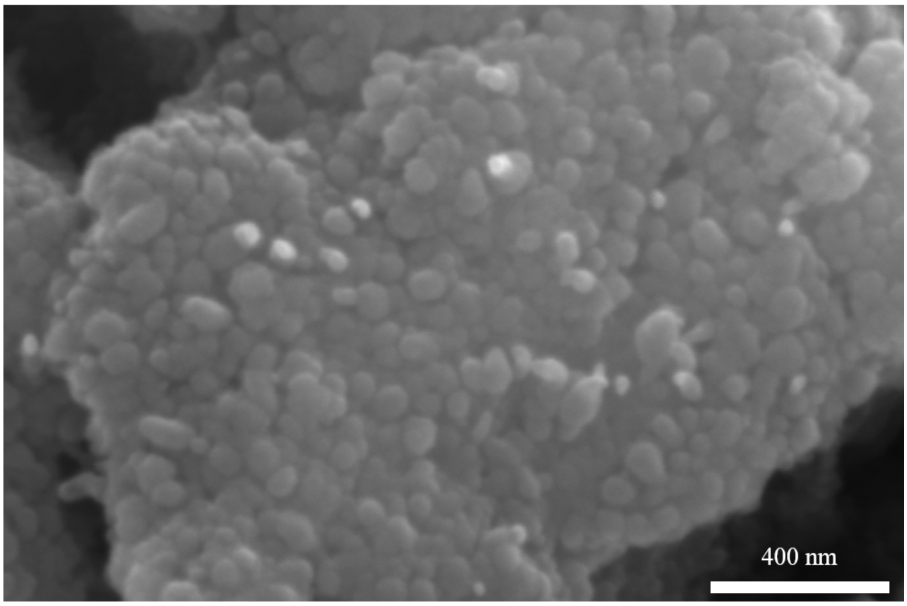


Fig. S15. SEM images of FeS_2@C electrode at the fully charged state after 1000 cycles

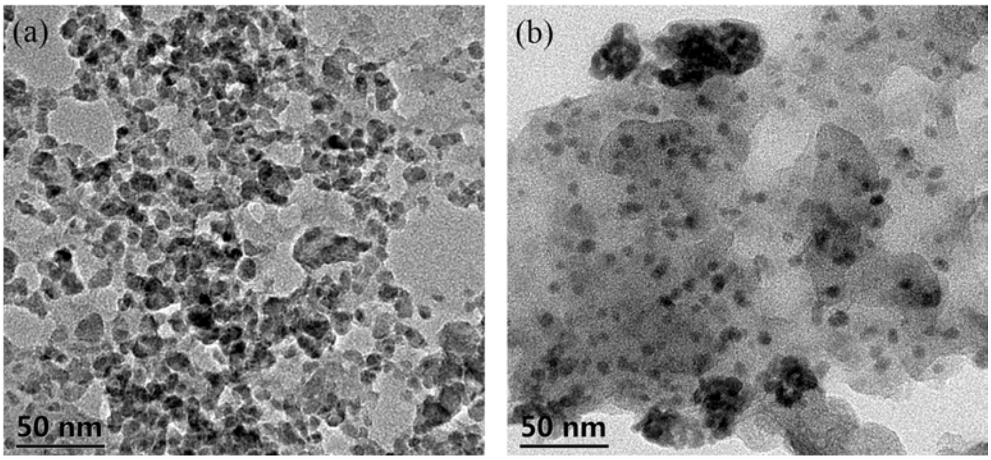


Fig. S16. TEM images of FeS_2@C electrode at the fully charged state: (a) pristine electrode, (b) electrode cycled after 1000 cycles