Supporting Information

Unoccupied 3d orbitals makes Li-unalloyable transition metals usable as anode materials for lithium ion batteries

Liping Guo,[a] Zhongqing Jiang[b] and Zhong-Jie Jiang[*c]

[a] *Guangzhou Key Laboratory for Surface Chemistry of Energy Materials, New Energy Research Institute, College of Environment and Energy, South China University of Technology, Guangzhou 510006, P. R. China. Email: eszjiang@scut.edu.cn and zhongjiejiang1978@hotmail.com*

[b] *Key Laboratory of Optical Field Manipulation of Zhejiang Province, Department of Physics, Zhejiang Sci-Tech University, Hangzhou 310018, P. R. China.*

[c] *Guangdong Engineering and Technology Research Center for Surface Chemistry of Energy Materials, College of Environment and Energy, South China University of Technology, Guangzhou 510006, P. R. China.*

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Figures. S1 to **S10**

Tables S1-S2

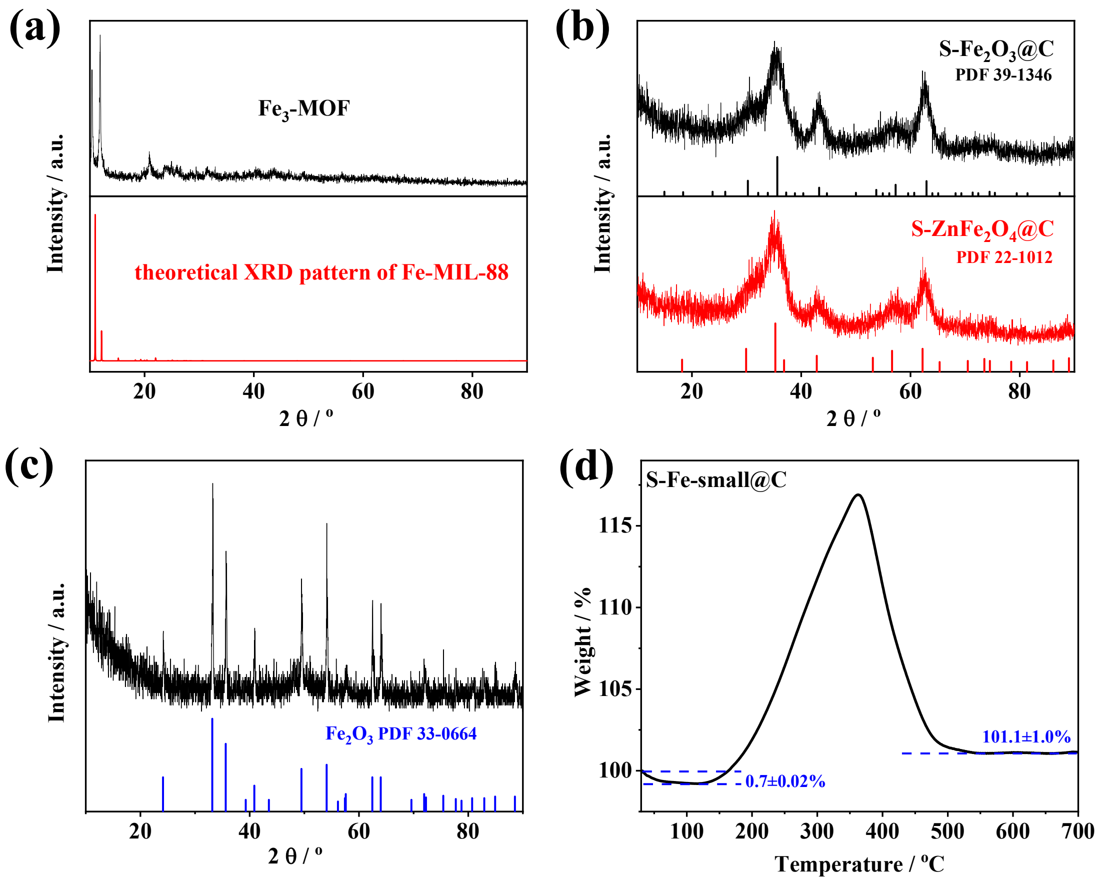


Figure S1. (a) XRD pattern of the Fe$_3$-MOF and standard XRD pattern of Fe-MIL-88. (b) XRD pattern of S-Fe_2O_3@C and S-$ZnFe_2O_4$@C. (c) XRD pattern of S-Fe@C after TG. (d) TG curve of the S-Fe-small@C.

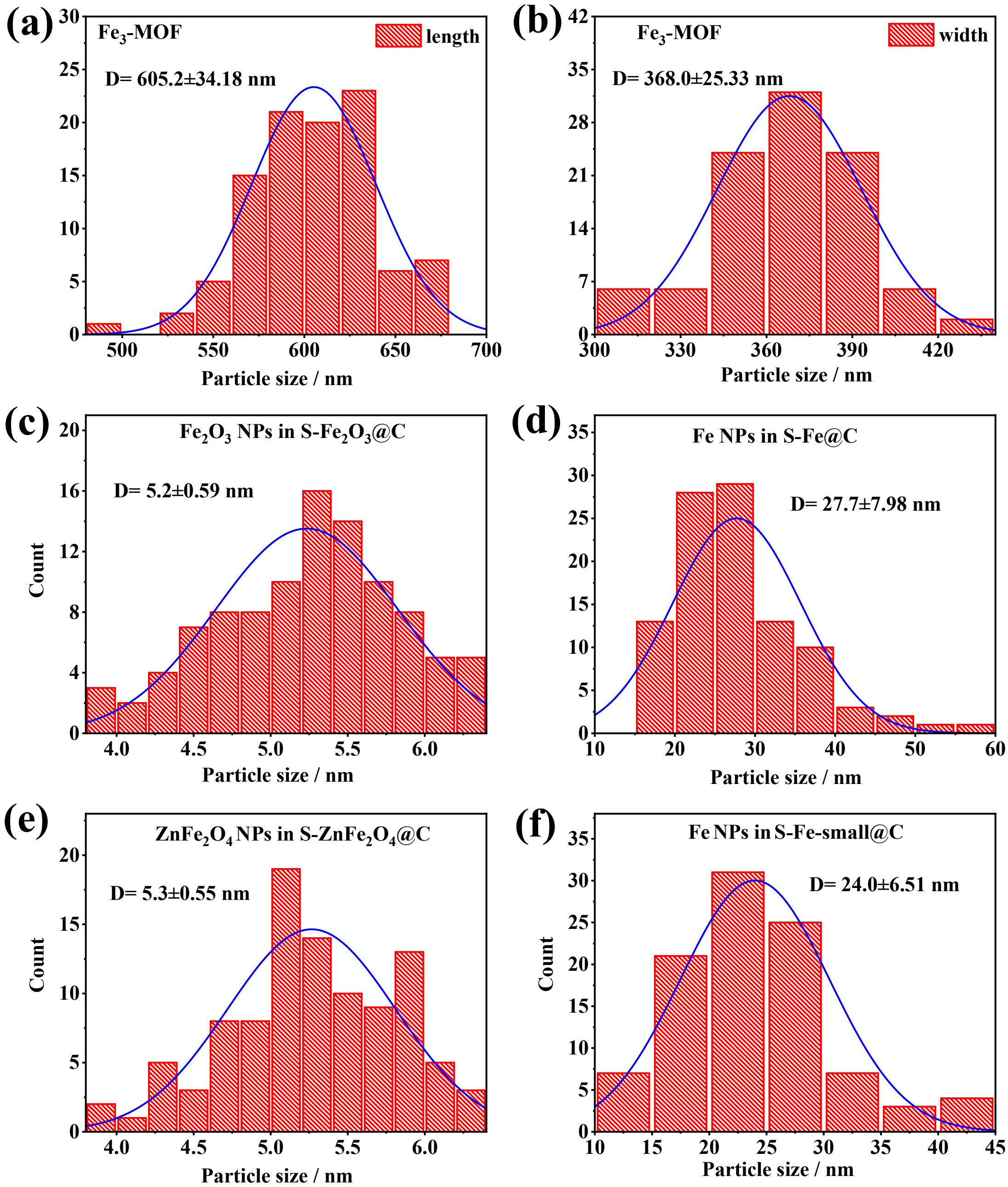


Figure S2. Particle size distribution of (a) and (b) Fe_3-MOF, (c) Fe_2O_3 NPs in the S-Fe_2O_3@C, (d) Fe NPs in the S-Fe@C, (e) $ZnFe_2O_4$ NPs in the S-$ZnFe_2O_4$@C and (f) Fe NPs in S-Fe-small@C.

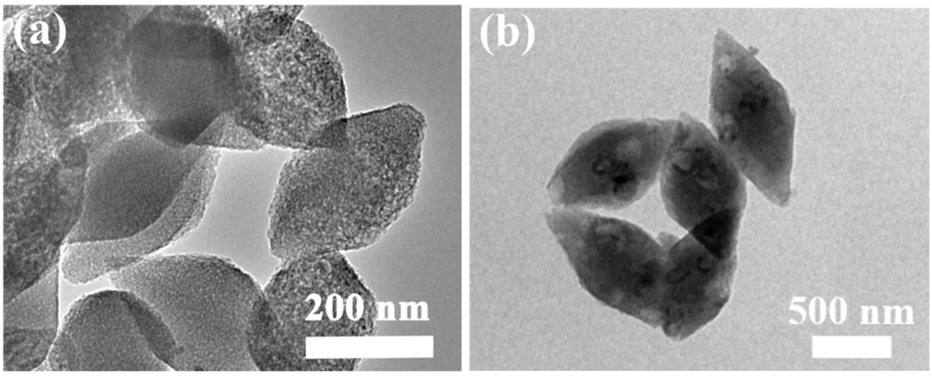
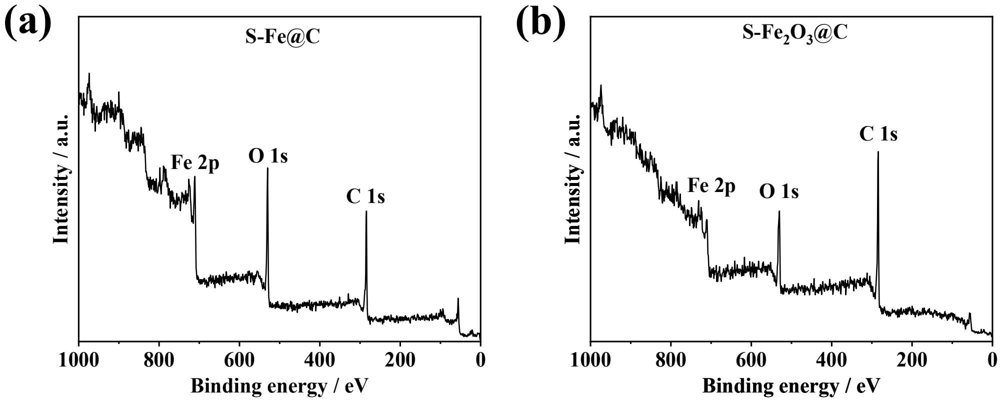


Figure S3. TEM images of (a) the porous carbon obtained by the removal of the Fe_2O_3 nanoparticles from the S-Fe_2O_3@C, and (b) the S-carbon synthesized by the removal of Fe from the S-Fe@C through the HCl etching.



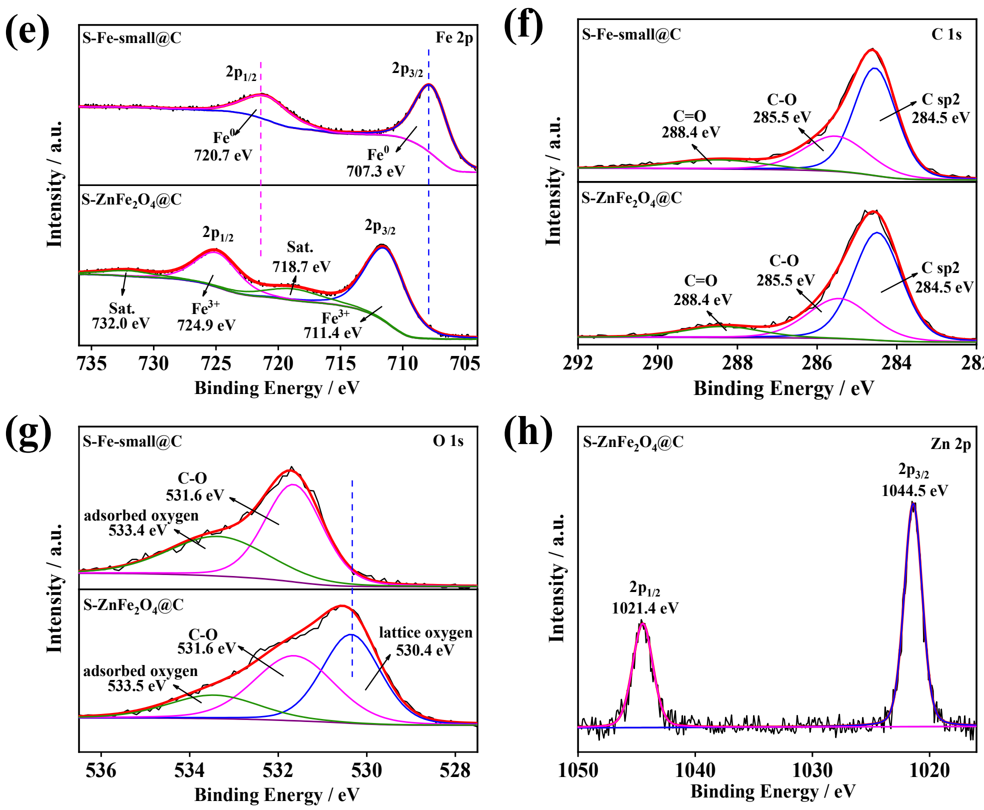


Figure S4. XPS survey spectra of (a) S-Fe@C, (b) S-Fe_2O_3@C, (c) S-$ZnFe_2O_4$@C and (d) S-Fe-small@C. High-resolution XPS spectra of (e) Fe 2p, (f) C 1s, and (g) O 1s for S-$ZnFe_2O_4$@C and S-Fe-small@C. (h) High-resolution XPS spectra of Zn 2p for S-$ZnFe_2O_4$@C.

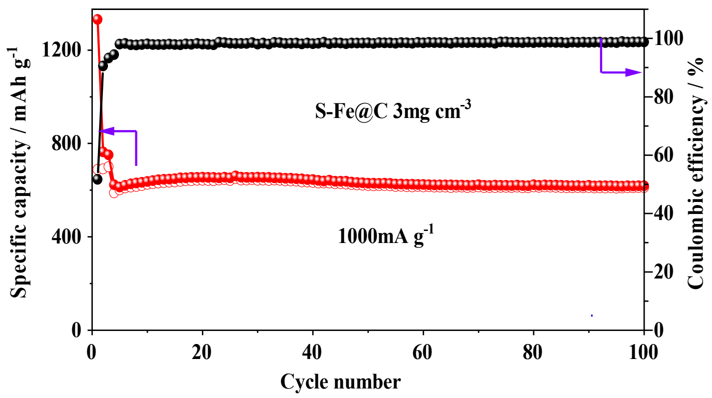


Figure S5. Cycling performance and coulombic efficiencies of S-Fe@C with a mass loading ~3.0 mg cm^{-2} at 1.0 A g^{-1}.

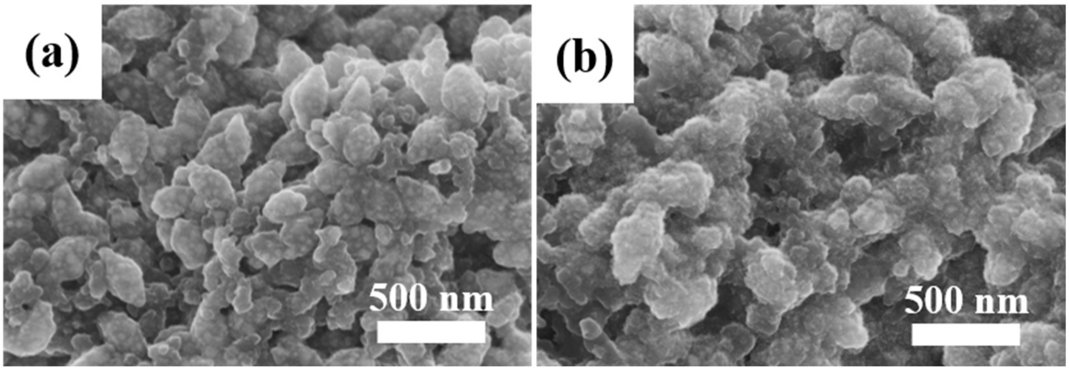


Figure S6. SEM image of S-Fe@C in the presence of carbon black and PVDF binders before and after 50 cycles at 1.0 A g^{-1}. The presence of carbon black and PVDF binders makes the profile of the particles less distinct.

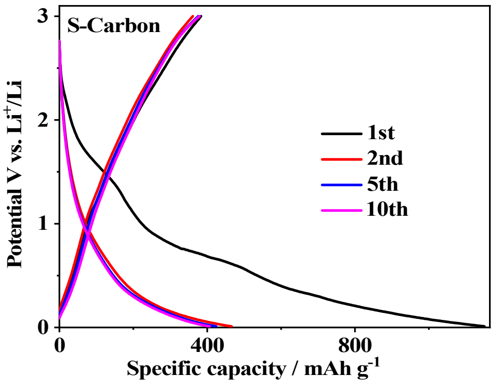


Figure S7. Charge/discharge voltage profiles of S-carbon at 100 mA g^{-1}.

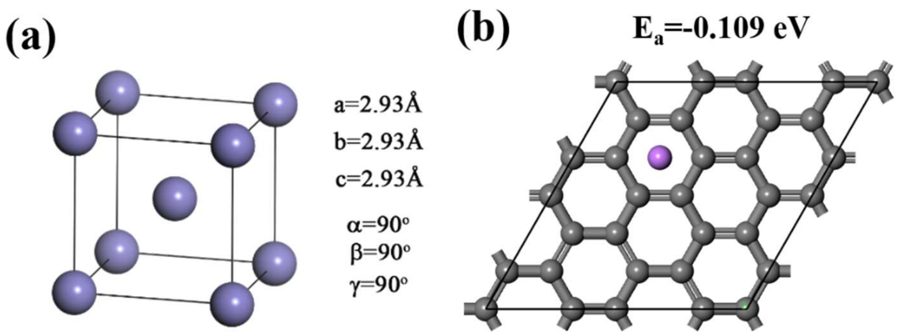


Figure S8. (a) Lattice constants of the cubic structure Fe. (b) Adsorption of the Li atom on a single layer graphene.

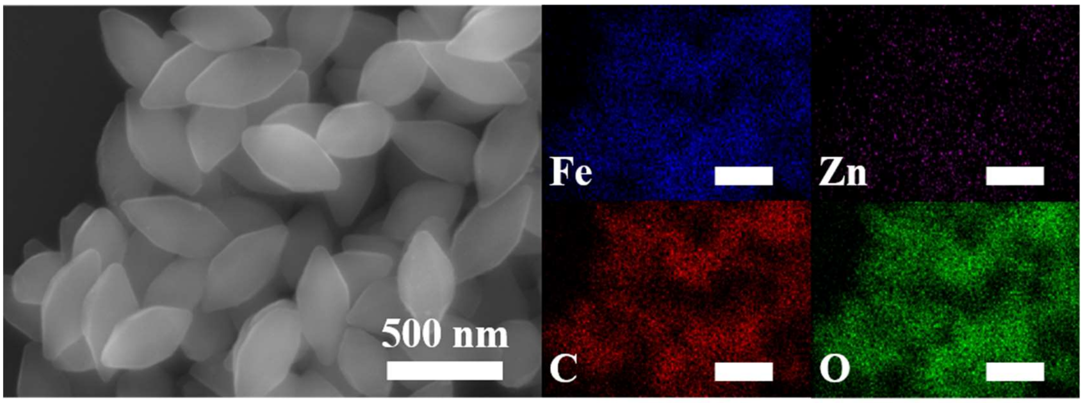


Figure S9. Elemental mapping images of S-$ZnFe_2O_4$@C.

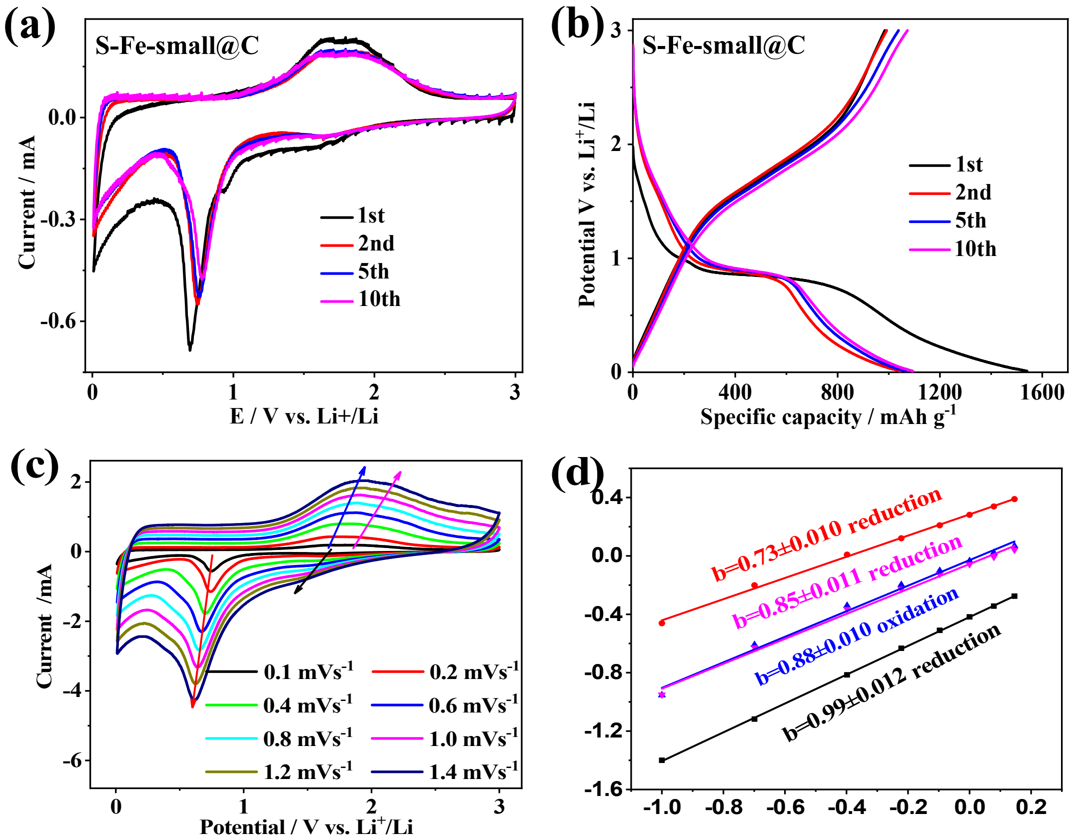


Figure S10. (a) CVs of S-Fe-small@C at 0.1mV s^{-1}. (b) Charge/discharge voltage profiles of (b) S-Fe-small@C. (c) CVs of S-Fe-small@C at different scan rates. (d) b-value of S-Fe-small@C.

Table S1. Stable reversible capacity comparison of the S-Fe@C and S-Fe-small@C with other anode materials for LIBs.

Electrode material	Mass loading mg cm^{-2}	Current density (mA g^{-1})	Cycles	Capacity (mAh g^{-1})	Reference
S-Fe@C	~1.0	100	100	967.3±16.2	This work
		1000	1000	700.4±10.5	
	~3.0	1000	100	611.0±10.5	
S-Fe-small@C	~1.0	100	100	1091.9±17.6	This work
		1000	1000	925.1±13.7	
Sb@C		1000	300	405	1
Sn@aCT	1.5	100	350	870	2
TiO_2-Sn@CNFs		200	1100	643	3
Sn-Sb micro/nano-structures	1.0	100	100	751	4
Sb/Sb_2O_3/CNT/GNR	0.9-1.1	50	100	619	5
SnSe/SnOx@CNFs	1.73	200	70	740.7	6
Sb_2Se_3	1.1	1000	1000	260.8	7
$SnSe_{0.5}S_{0.5}$/C	1.0	200	150	785	8
Bi_2S_3@C NW	1.0-1.5	1000	700	501	9
Bi_2S_3@Co_9S_8	0.9-1.2	100	100	798	10
Fe-MIL-88 B	1	60	400	744.5	11
Fe-BTC	2	1000	400	408.8	12
MIL-53(Fe) @RGO	0.75	100	100	550	13
Mg-MOF-74/Cu	1.0-1.5	500	300	531.7	14
Fe_2O_3@PAN	0.6-0.8	1000	500	506.6	15
Fe_3O_4/C@VO_x	1.2	1000	500	845	16
C@Fe_3C/Fe	1.5	2000	1000	392	17
Fe_3N@C	0.6-1.2	100	500	358	18
Ge_3N_4@C	3.5	550	200	702	19
N-Ti_3C_2/Fe_2O_3	1.5	2000	400	549	20
Co_3O_4@$Co_3V_2O_8$	0.8	100	100	948	21
$ZnMn_2O_4$	1.0	200	100	867	22
Zn_2SiO_4@NC	2.0	1000	400	540	23
NiSx@C	1.0	1000	2000	460	24
CoS_2/CNTs/graphene	2.0	100	100	368.2	25
NHMCFs/$MoSe_2$		1000	400	582.5	26
ZnS/NC	1.5-2.0	200	100	757	27
Ni_2P/Ni	1.5	1000	1000	597	28
Ni_2Pp⊂GN		100	250	511	29
FeS_2/Fe_7S_8-rGO	1.0	200	250	650	30
GeP_3/C	1.3	1000	1000	312	31
CoP@C		1000	800	500	32
MoS_2/Mo_2TiC_2Tx		100	100	509	33
$(FeCoNiCrMn)_3O_4$	~3.0	500	300	402	34
Fe-BTC	2.0	1000	400	408.8	12
Zn_2SiO_4@NC	2.0	1000	400	540	23
CoS_2/CNTs/graphene	2.0	100	100	368.2	25
VN nanosheet	2.0	100	100	520	35

Table S2. Rate performance comparison of the S-Fe@C and S-Fe-small@C with other anode materials for LIBs.

Electrode material	Mass loading mg cm^{-2}	0.1 A g^{-1}	0.2 A g^{-1}	0.5 A g^{-1}	1.0 A g^{-1}	2.0 A g^{-1}	5.0 A g^{-1}	10.0 A g^{-1}	Reference
S-Fe@C	~1.0	851.0 ±12.9	825.9 ±12.5	809.0 ±12.1	762.6 ±11.4	666.8 ±10.3	534.4 ±8.3	410.1 ±6.6	This work
S-Fe-small@C	~1.0	1092.9 ±17.9	1046.2 ±16.5	971.9 ±16.1	900.2 ±14.3	815.7 ±12.2	659.5 ±9.8	490.6 ±7.7	This work
Sb@C		623	558	496	439	385			1
TiO_2-Sn@CNFs			570		280				3
Sn-Sb micro /nano structures	1.0	798.8	717.8	636.5	545.5	455.0			4
Sb/Sb_2O_3/CNT /GNR	0.9-1.1	642	514	428	369	327			5
SnO_2@SnS_2@NG		898	820	715	612	497	343		36
SnSe/SnOx@C NFs	1.73	803	709	579	391	301			6
Sb_2Se_3	1.1	638.2	611.5	543.6	472.3	389.5			7
$SnSe_{0.5}S_{0.5}$/C	1.0	989	830	729	646	553	389		8
Bi_2S_3@Co_9S_8	0.9-1.2	785	672	612	573	512			10
MoS_2@SnS-QDs/CNN	1.0-1.2	1130	1078	947	765	591			37
C@Fe_3C/Fe	1.5	1177	1012	954	845	682	521		17
Co_3O_4@ $Co_3V_2O_8$	0.8	1068	916	782	678	578	550		21
PCN-600(iron porphyrin-based MOF)	0.5				625	470			38
Fe-MIL-88 B	1	692.0	582.6	350.4	232.7	143.5	133.4		11
Fe-BTC	2	873.8 /915.7	990.1 /996.3		523.2 /525.0	302.8 /304.8			12
MIL-53(Fe) @RGO	0.75	510		400	360	300			13
Mg-MOF-74/Cu	1.0-1.5	796.2		560.5	372.6	259.1			14
NiO@N-C		1065	1031		689	634			39
Fe_3O_4/C@VO_x	1.2		810	718	605	483	340		16
Fe_2N@C	1.4-2.1	567	526	500	474	450	404	356	40
Fe_3O_4 nanoparticle		1084	883	809	648	545	410		41
$ZnMn_2O_4$	1.0	857	784	636	481	355	94	36	22
Zn_2SiO_4@NC	2.0	640	620	560	450	370	280		23
NiSx@C	1.0	790	720	605	540	446	350	280	24
CoS_2/CNTs /graphene	2.0		381			251	212		25
NHMCFs /$MoSe_2$		666.4	635.3	352.9				244.3	26
ZnS/NC	1.5-2.0	771	725		600	511			27
MoS_2 /Mo_2TiC_2Tx		523	484	407	315	182			33
$NiCoPS_3$/NC	0.9-1.2	976	781	723	665	625	570		42
Ni_2P/Ni	1.5	611	583	521	483	449			28
Ni_2Pp⊂GN		520	449	397	291	283	246		29
CoP@C		770	690	560	490	420	340		32

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