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Supporting Information

$Fe(CN)_6^{3-}$ Ions-Modified MnO_2/Graphene Nanoribbons Enabling High Energy Density Asymmetric Supercapacitors

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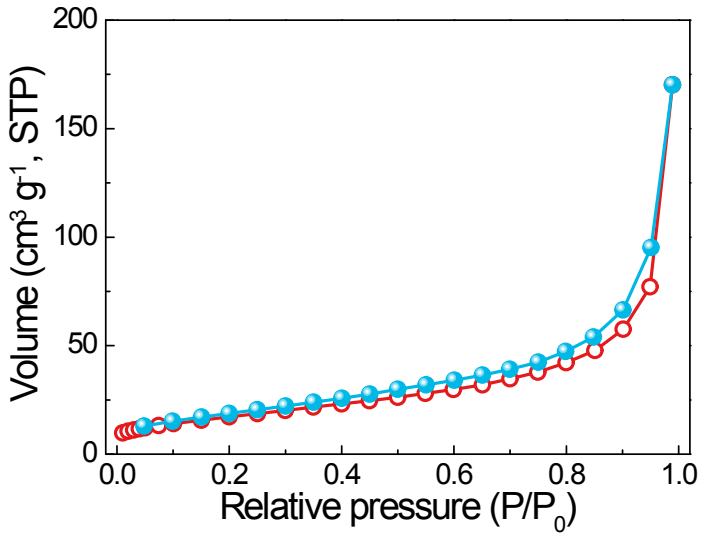

Fig. S1. Nitrogen adsorption and desorption isotherms of the MnO_2/GR

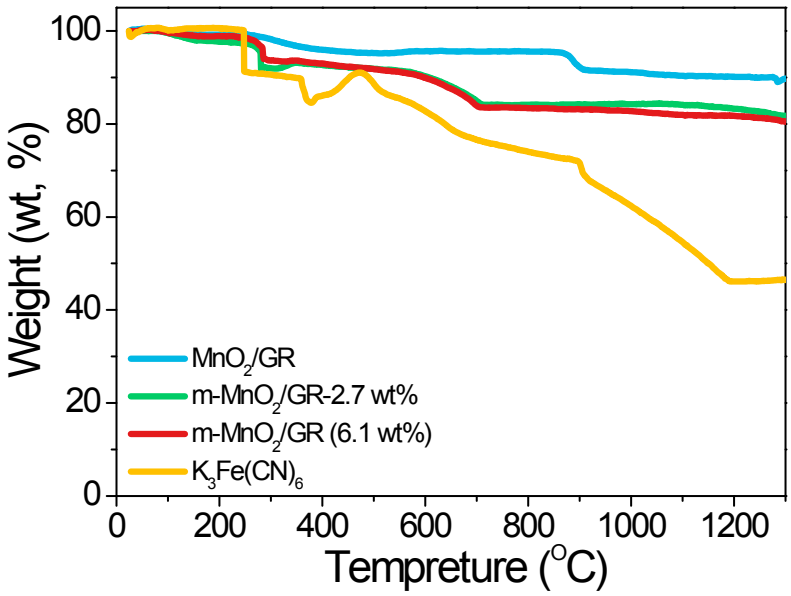

Fig. S2. TGA curves the m-MnO_2/GR (6.1wt%), m-MnO_2/GR-2.7wt%, MnO_2/GR and $K_3Fe(CN)_6$ in air with a temperature range from 25 to 1300 °C. For MnO_2/GR TGA curve, the final product Mn_3O_4 is 89.7.[1] From the TGA curve of m-MnO_2/GR, if we assume that the total mass is 100, and the GR, MnO_2 and $K_3Fe(CN)_6$ are x, y and z, respectively, combined with TGA curve of $K_3Fe(CN)_6$, the following formulas are ture:

$$\begin{aligned} &x+y+z=100 \\ &y=19x \\ &0.87y+0.465z=80.45 \end{aligned} \qquad \text{The result is} \qquad \begin{aligned} &x=4.7 \\ &y=89.2 \\ &z=6.1 \end{aligned}$$

That is to say, the GR, MnO_2 and $K_3Fe(CN)_6$ contents are 4.7, 89.2 and 6.1 wt%, respectively.

Table S1. Comparison of the m-MnO_2/GR with previously reported MnO_2-based electrodes in concern of the specific capacitance.

Materials	Capacitance (F g^{-1})	Ref.
MnO_2 nanosheet	300	[2]
MnO_2 nanowires	340	[3]
Hierarchical porous C/MnO_2	392	[4]
MnO_2/C	288	[5]
rGO/MnOx	202	[6]
MnO_2/GO	297	[7]
MnO_2/Ti_3C_2	390	[8]
Metal−organic framework structure (NiHCF)/MnO_2	224	[9]
Manganese hexacyanoferrate/MnO_2	225.6	[10]
Ag/MnO_2	198.9	[11]
Silicon diatom@MnO_2	341.5	[12]
$Ni(OH)_2$/MnO_2 core–shell nanowires	355	[13]
m-MnO_2/GR	**435**	**This work**

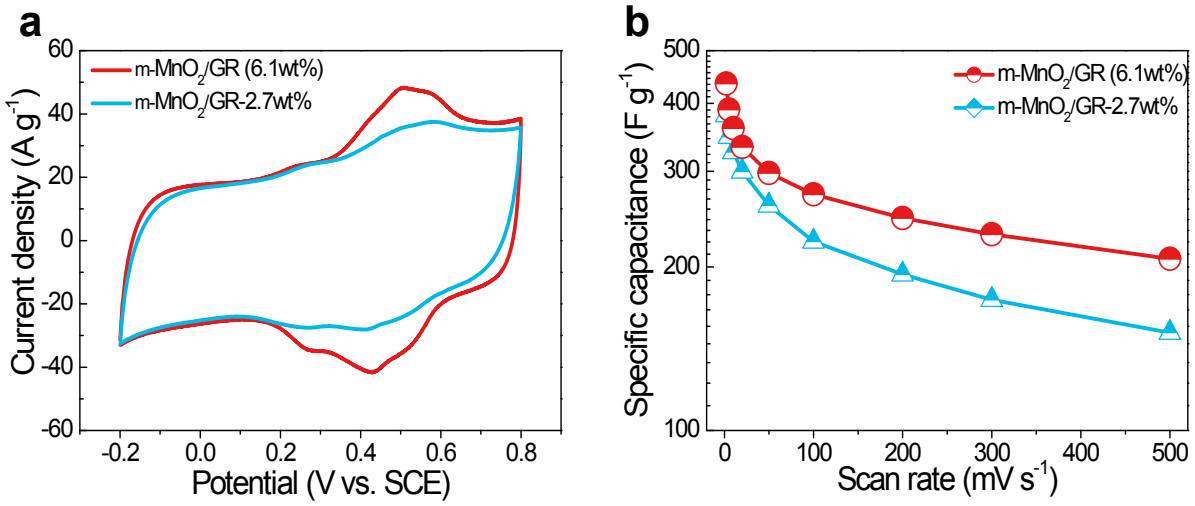

Fig. S3. (a) CV curves of the m-MnO_2/GR (6.1wt%) and m-MnO_2/GR-2.7wt% electrodes at 100 mV s^{-1}. (b) Specific capacitances of the m-MnO_2/GR (6.1wt%) and m-MnO_2/GR-2.7wt% electrodes.

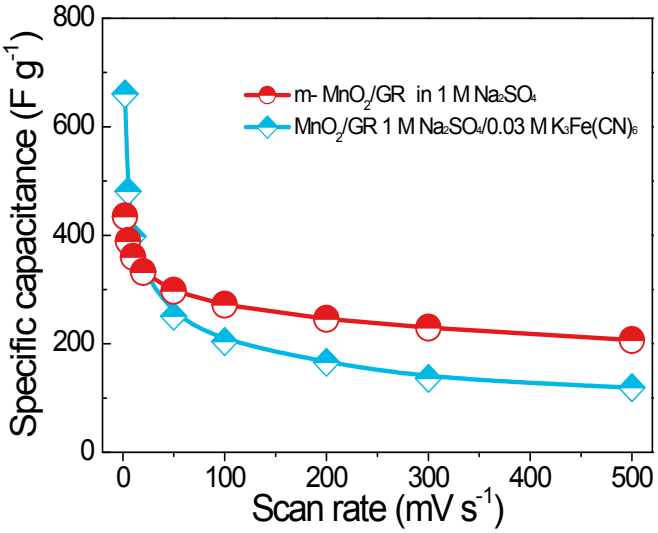

Fig. S4. Specific capacitances of the m-MnO_2/GR electrode in 1 M Na_2SO_4 electrolyte and MnO_2/GR in 1 M Na_2SO_4/0.03 M $K_3Fe(CN)_6$ electrolyte.

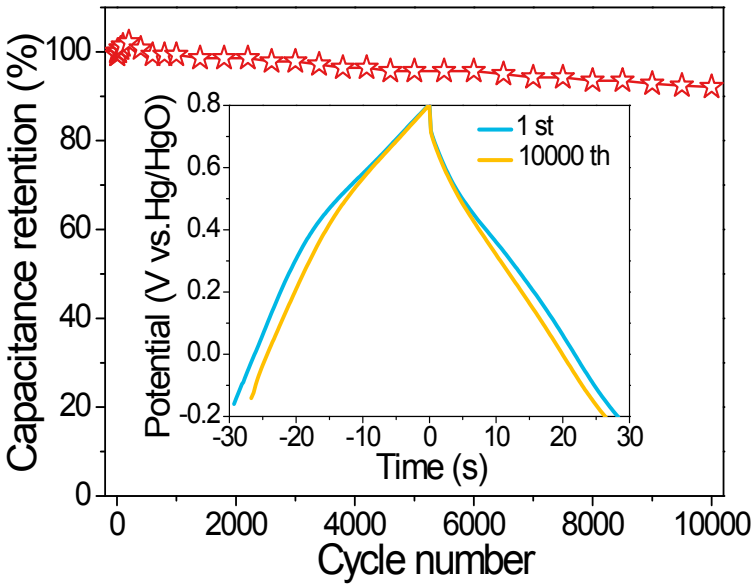

Fig. S5. Cycling performance of the m-MnO_2/GR electrode measured at 20 A g^{-1} for 10 000 cycles.

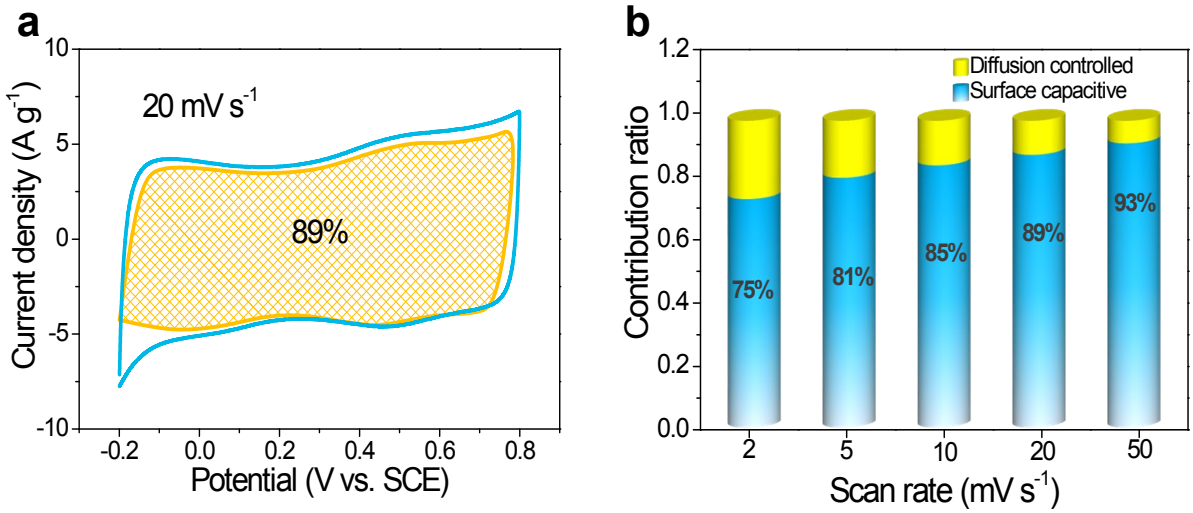

Fig. S6. (a) Separation of the capacitive (shaded region) and diffusion currents in the MnO_2/GR at a scan rate of 20 mV s^{-1}. (b) Contribution ratio of the diffusion-controlled and capacitance-controlled charges at different scan rates.

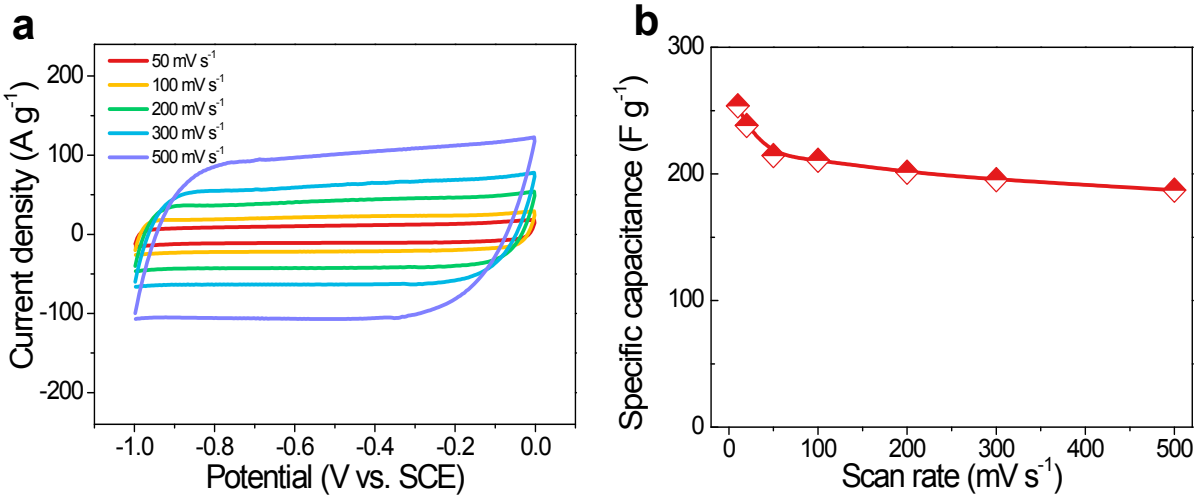

Fig. S7. Electrochemical performances of the GR electrode using a three-electrode cell in 1M Na_2SO_4 electrolyte within a potential window of -1 to 0 V (vs. SCE). (a) CV curves of the GR at various scan rates in 1 M Na_2SO_4 electrolyte. (b) Specific capacitances of the GR electrode.

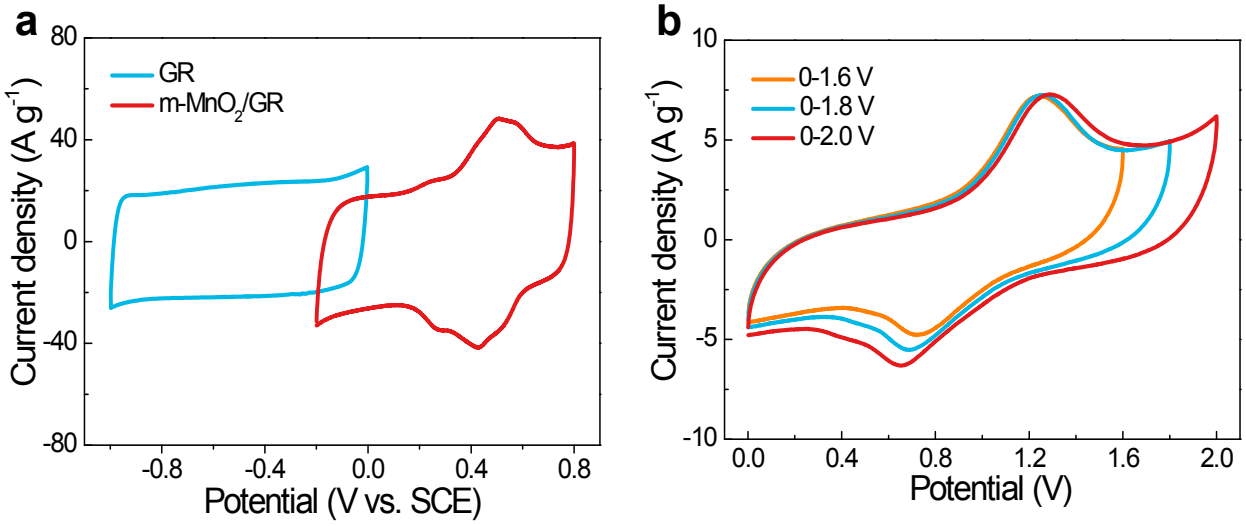

Fig. S8. (a) CV curves of the GR and m-MnO_2/GR in a three-electrode cell at 100 mV s^{-1}. (b) CV curves of m-MnO_2/GR//GR ASC operated in different voltage windows at 50 mV s^{-1}.

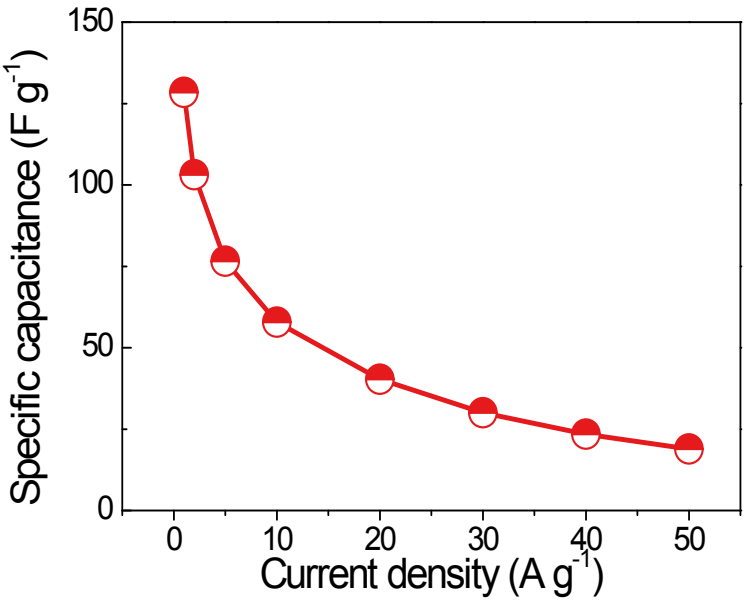

Fig. S9. Gravimetric specific capacitances of the m-MnO_2/GR//GR ASC at various current densities ranging from 1 to 50 A g^{-1}.

Table S2. Comparison of the m-MnO_2/GR//GR ASC with previously reported MnO_2-based ASCs in aqueous electrolytes.

Electrode materials		Electrolyte	Voltage	E	P	Ref.
Anode	Cathode		(V)	(Wh kg^{-1})	(W kg^{-1})	
N-doped hollow carbon spheres(NHCSs)	MnO_2/NHCSs	1 M Na_2SO_4	1.8	26.8	233	[4]
Activated graphene oxide	Si-diatom@MnO_2	1 M Na_2SO_4	1.6	23.2	120	[12]
TiO_2	MnO_2	1 M $LiClO_4$	2.0	7.7	762.5	[14]
Three-dimensional N-doped reduced graphene oxide (3D-NRGO)	MnO_2/3D-NRGO	1 M Na_2SO_4	2.0	35.28	200	[15]
Nitrogen-doped porous carbon	Porous carbon@MnO_2	1 M Na_2SO_4	1.8	34.7	1000	[16]
Hierarchical porous carbon (HPC)	MnO_2/GO	1 M Na_2SO_4	2.0	46.7	100	[7]
Cross-linked carbon nanosheets (CCNs)	MnO_2@CCNs	1 M Na_2SO_4	1.9	23.6	188.8	[17]
Microwave exfoliated graphite oxide	MnO_2 nanosheets arrays	1 M Na_2SO_4	1.6	25.8	400	[18]
N-doped carbon	MnO_2/C	1 M Na_2SO_4	2.0	39.5	200	[5]
Polypyrrole(PPy)	MnO_2	1 M Na_2SO_4	1.7	27.2	850	[19]
p-BC/N-5M	p-BC@MnO_2-2h	1 M Na_2SO_4	2.0	32.9	285	[20]
Graphene/MoO_3	Graphene/MnO_2	1 M Na_2SO_4	2.0	42.6	276	[21]
CNT	MnO_2	1 M Na_2SO_4	2.0	47.4	200	[22]
Graphene	Graphene/MnO_2	1 M Na_2SO_4	2.0	30.4	100	[23]
ACF	Graphene/MnO_2	1 M Na_2SO_4	1.8	51.1	102	[24]
Graphene hydrogel	MnO_2	0.5M Na_2SO_4	2.0	23.2	1000	[25]

Electrode materials		Electrolyte	Voltage	E	P	Ref.
Anode	Cathode		(V)	(Wh kg^{-1})	(W kg^{-1})	
Activated graphene	Activated graphene/MnO_2	1 M Na_2SO_4	2.0	24.3	24500	[26]
Carbon spheres	Carbon spheres/MnO_2	1 M Na_2SO_4	2.0	22.1	7000	[27]
CNT/In_2O_3	CNT/MnO_2	1 M Na_2SO_4	2.0	25.5	30000	[28]
E-CMG	E-CMG/MnO_2	1 M Na_2SO_4	2.0	44	11200	[29]
CNT/V_2O_5	MnO_2/carbon	1 M Na_2SO_4	1.6	16	75	[30]
SWNTs	Graphene/MnO_2	0.5M Na_2SO_4	1.5	12.5	80000	[31]
Graphene/Ag	Graphene/MnO_2	1 M Na_2SO_4	1.8	50.8	101.5	[32]
AC	AC/MnO_2	0.5M Na_2SO_4	1.8	10.4	14700	[33]
Graphene	Graphene/MnO_2	1 M Na_2SO_4	1.7	21.3	250	[34]
AC	MnO_2	2 M $CaSO_4$	2.0	22.5	1000	[35]
AC	AC/MnO_2	0.5M Na_2SO_4	2.0	18.2	10100	[36]
GR	**m-MnO_2/GR**	**1 M Na_2SO_4**	**1.8**	**57.8**	**1200**	**This work**

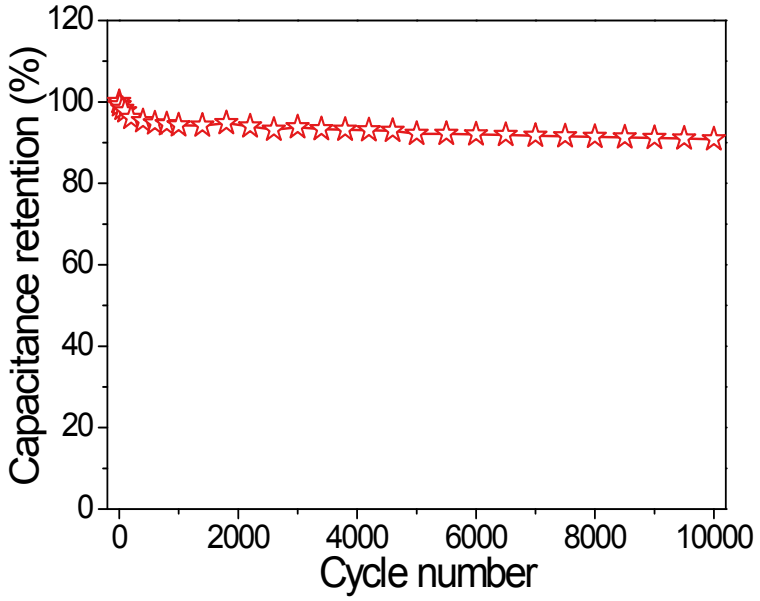

Fig. S10. Cycling performance of the MnO_2/GR//GR ASC.

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