



Supplementary Materials

# Facile Fabrication of $\text{MnO}_2$ /Graphene/Ni Foam Composites for High-Performance Supercapacitors

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**Table S1.** The mass of graphene and MnO<sub>2</sub> loaded on the MnO<sub>2</sub>/graphene/Ni sample by electrodeposition at different current densities.

	Blank Ni foam (mg)	Graphene loaded (mg)	MnO <sub>2</sub> loaded (mg)	Total loaded Weight (mg)	Ni: graphene: MnO <sub>2</sub> (mass ratio)
1 mA/cm <sup>2</sup>	51.25(±2.56)	<b>0.12(±0.01)</b>	<b>0.09(±0.01)</b>	<b>0.21(±0.02)</b>	1: 0.002: 0.002
5 mA/cm <sup>2</sup>	55.62(±2.22)	0.15(±0.02)	0.12(±0.02)	0.27(±0.04)	1: 0.003: 0.002
10 mA/cm <sup>2</sup>	50.62(±3.50)	0.13(±0.01)	0.18(±0.02)	0.31(±0.03)	1: 0.003: 0.004
15 mA/cm <sup>2</sup>	54.35(±2.72)	0.14(±0.02)	0.25(±0.03)	0.39(±0.05)	1: 0.003: 0.005

**0.12(±0.01) mg, 0.09(±0.01) mg and 0.21(±0.02) mg** were obtained by statistical analysis method as follows.

For example, the MnO<sub>2</sub>/graphene/Ni foam electrode prepared at 1 mA/cm<sup>2</sup>, the mass of graphene loaded was measured 5 times by ultra-precise balance. The mass of loaded graphene was 0.10 mg, 0.12 mg, 0.13 mg, 0.13 mg, and 0.14 mg, respectively. The data are calculated by statistical method as follows.

The experimental data is expressed as follows:

$$x = \bar{X} \pm \sigma_{\bar{x}}$$

x: Results of multiple mass weighing

$\bar{X}$  : mean of measured data

$\sigma_{\bar{x}}$ : standard error of the mean

$$\begin{aligned}\bar{X} &= (0.10 + 0.12 + 0.13 + 0.13 + 0.14) \div 5 \\ &= 0.12\end{aligned}$$

For a limited number of mass weighing, n= 5

$$\sigma_{\bar{x}} = \sqrt{\frac{\sum d_i^2}{n(n-1)}}$$

$$d = x - \bar{x}$$

$$\begin{aligned}\sigma_{\bar{x}} &= \sqrt{\frac{(0.10-0.12)^2 + (0.12-0.12)^2 + (0.13-0.12)^2 + (0.13-0.12)^2 + (0.14-0.12)^2}{5 \times (5-1)}} \\ &= 0.01\end{aligned}$$

$$x = \bar{X} \pm \sigma_{\bar{x}}$$

$$= \mathbf{0.12 \pm 0.01 \text{ mg}}$$

For example, the MnO<sub>2</sub>/graphene/Ni foam electrode prepared at 1 mA/cm<sup>2</sup>, the mass of coated MnO<sub>2</sub> was also measured 5 times by ultra-precise balance. MnO<sub>2</sub> loaded mass was 0.07 mg, 0.08 mg, 0.09 mg, 0.10 mg, and 0.12 mg, respectively. The experimental data is calculated as follows:

$$\bar{X} = (0.07 + 0.08 + 0.09 + 0.10 + 0.12) \div 5$$

$$= 0.09$$

For a limited number of measurements, n= 5

$$\sigma_{\bar{x}} = \sqrt{\frac{\sum d_i^2}{n(n-1)}}$$

$$d = x - \bar{x}$$

$$\begin{aligned}\sigma_{\bar{x}} &= \sqrt{\frac{(0.07-0.09)^2 + (0.08-0.09)^2 + (0.09-0.09)^2 + (0.10-0.09)^2 + (0.12-0.09)^2}{5 \times (5-1)}} \\ &= 0.01\end{aligned}$$

$$x = \bar{X} \pm \sigma_{\bar{x}}$$

$$= \mathbf{0.09 \pm 0.01 \text{ mg}}$$

### Total mass loaded

$$\begin{aligned}m_t &= m_g + m_{\text{MnO}_2} \\&= 0.12 + 0.09 \\&= \underline{0.21}\end{aligned}$$

Error limits of  $m_t$  from statistical analysis

$$\begin{aligned}&= 0.01 + 0.01 \\&= \underline{0.2}\end{aligned}$$

Hence,  $m_t = \underline{0.21 \pm 0.02 \text{ mg}}$

**Table S2.** The specific capacitances ( $C_s$ ,  $C_s'$  and  $C_{sA}$ ) of  $\text{MnO}_2/\text{graphene}/\text{Ni}$  foam prepared at different electrodeposition current densities obtained from CV curves under various scan rates.

Scan rate	Specific Capacitance											
	1 mA/cm <sup>2</sup>			5 mA/cm <sup>2</sup>			10 mA/cm <sup>2</sup>			15 mA/cm <sup>2</sup>		
	$C_s$ (F/g)	$C_s'$ (F/g)	$C_{sA}$ (mF/cm <sup>2</sup> )	$C_s$ (F/g)	$C_s'$ (F/g)	$C_{sA}$ (mF/cm <sup>2</sup> )	$C_s$ (F/g)	$C_s'$ (F/g)	$C_{sA}$ (mF/cm <sup>2</sup> )	$C_s$ (F/g)	$C_s'$ (F/g)	$C_{sA}$ (mF/cm <sup>2</sup> )
100 mV/s	202.9	179.3	36.5	155.8	138.5	38.4	76.7	89.1	27.6	52.4	67.2	26.2
80 mV/s	205.7	176.3	37.0	141.6	125.8	34.0	83.5	97.0	30.1	57.5	73.7	28.7
60 mV/s	214.3	183.7	38.6	170.0	151.1	40.8	91.4	106.1	32.9	63.5	81.4	31.7
40 mV/s	230.6	197.7	20.5	181.8	161.6	43.6	114.2	132.6	41.1	71.6	91.8	35.8
20 mV/s	261.6	224.2	47.1	202.0	179.6	48.5	122.9	142.7	44.2	86.3	110.6	43.1
10 mV/s	292.8	250.9	52.7	222.3	197.6	53.3	142.0	164.9	51.1	99.6	127.7	49.8

Notes:

(a)  $C_s$ : specific capacitance, calculated based on  $C_s = \int \frac{|i|dV}{2m_{\text{v}\Delta V}}$ ,  $m$  is the mass of deposited  $\text{MnO}_2$ .

(b)  $C_s'$ : specific capacitance, calculated based on  $C_s' = \int \frac{|i|dV}{M_{\text{v}\Delta V}}$ , and  $M$  is the mass of total loaded (graphene and  $\text{MnO}_2$ ).

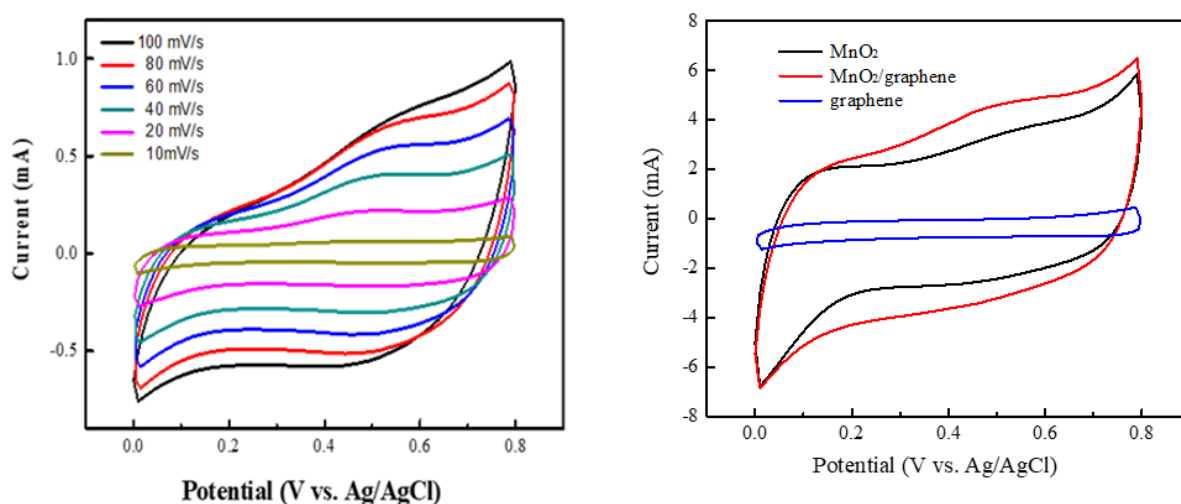
(c)  $C_{sA}$ : areal capacitances,  $C_{sA}' = \int \frac{|i|dV}{S_{\text{v}\Delta V}} = \frac{M}{s} \times \frac{1}{M} \int \frac{|i|dV}{\text{v}\Delta V} = C_s' \times \frac{M}{s}$

**Table S3.** The powder properties of  $\text{MnO}_2$  and  $\text{MnO}_2/\text{graphene}$  materials.

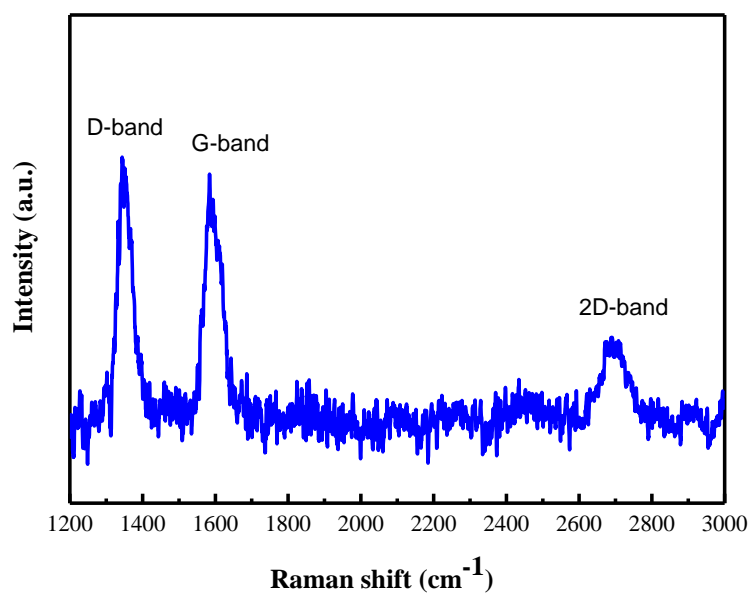
Materials	Surface area (m <sup>2</sup> .g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> . g <sup>-1</sup> )	Pore size (nm)
$\text{MnO}_2$	158.5	0.3	3.7
$\text{MnO}_2/\text{graphene}$	179.2	0.3	7.8

**Table S4.** A comparison of the energy density and power density for the MnO<sub>2</sub>//carbon system asymmetric supercapacitor in this work with the literature.

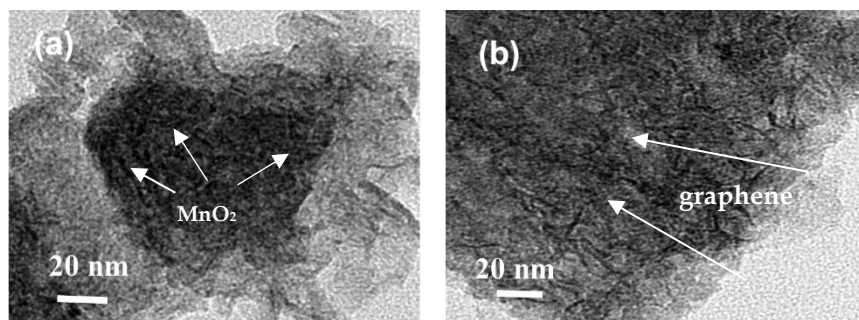
Materials	Electrolyte	Voltage Window (V)	Power Density (W/kg)	Energy Density (Wh/kg)	Reference
Zn-K-ATC/MnO <sub>2</sub> //Zn-K-ATC	1 M Na <sub>2</sub> SO <sub>4</sub>	0–2.0	1000	46	42
MnO <sub>2</sub> -GM-13-Ni//GM-13-Ni	1 M Na <sub>2</sub> SO <sub>4</sub>	0–2.0	500	125	43
GR/MWCNT/MnO <sub>2</sub> //GR/MWCNT/MnO <sub>2</sub>	0.5 M Na <sub>2</sub> SO <sub>4</sub>	0–1.8	426	35.5	44
N/P-HCS@MnO <sub>2</sub> -30//N/P-HCS	1 M Na <sub>2</sub> SO <sub>4</sub>	0–1.8	449.8	32.2	45
GdMnO <sub>2</sub> /Ni(OH) <sub>2</sub> //PVA/KOH//Fe <sub>3</sub> O <sub>4</sub> /GO	PVA/KOH	0–1.6	2332	60	46
rGO/MnO <sub>x</sub> //AC	[C <sub>2</sub> MI <sub>m</sub> ]BF <sub>4</sub>	0–2.7	200	50	47
NiCo <sub>2</sub> S <sub>4</sub> /Co <sub>9</sub> S <sub>8</sub> //AC	1 M KOH	0–1.6	800	36.7	48
MnO <sub>2</sub> /graphene//graphene	0.5 M Na <sub>2</sub> SO <sub>4</sub>	0–0.8	400	91	This work



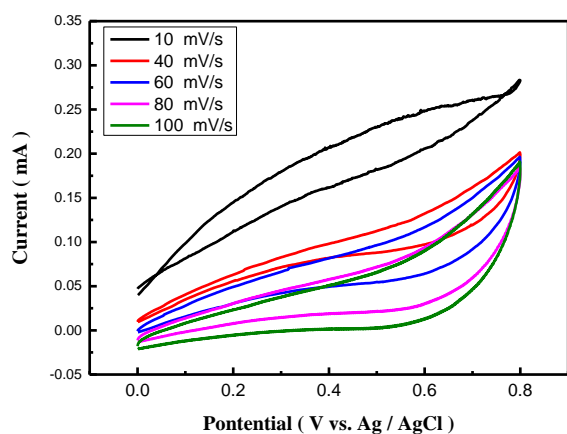
**Figure S1.** (a) CV curves of 0.12 mg loaded graphene/Ni at different scan rates; (b) CV curves of MnO<sub>2</sub>, MnO<sub>2</sub>/graphene/Ni and graphene/Ni (Ni: 54.35 mg, MnO<sub>2</sub>: 0.09 mg, and graphene: 0.12 mg).



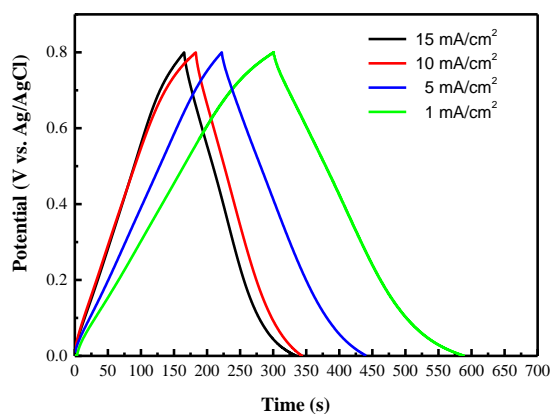
**Figure S2.** The Raman spectra of as-produced graphene.



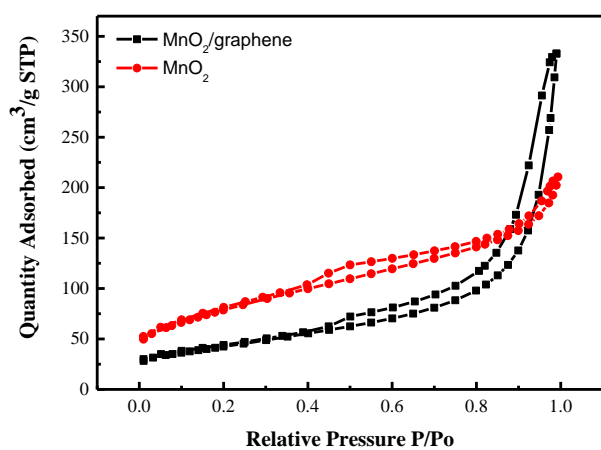
**Figure S3.** The TEM analysis for the as-obtained MnO<sub>2</sub> (a) and MnO<sub>2</sub>/graphene material (b).



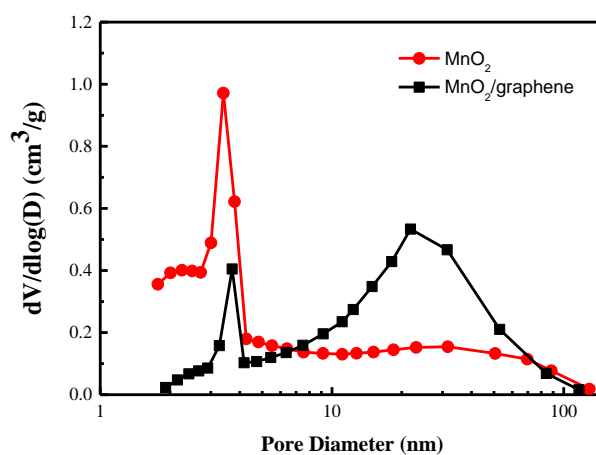
**Figure S4.** The CV characteristic curves of blank Ni foam at different scan rates.



**Figure S5.** The GCD test for MnO<sub>2</sub>/graphene/Ni electrodes obtained from different electrodeposition current densities examined at 1 A g<sup>-1</sup>.



(a)



(b)

**Figure S6.** BET specific surface area and pore size distribution analysis for MnO<sub>2</sub> and MnO<sub>2</sub>/graphene materials. (a) N<sub>2</sub> isotherm adsorption-desorption analysis and (b) pore distribution analysis.