Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
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Electronic Supplementary Information for:

Porphyrin-graphene oxide frameworks for long life sodium ion batteries

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Experimental section

***Synthesis of 5,10,15,20-tetrakis(3',4'-dimethoxyphenyl)porphyrin**:* 3,4-dimethoxy benzaldehyde (5g, 30 mmol) was dissolved in 200 ml of propionic acid and refluxed at 120°C, followed by addition of freshly distilled pyrrole (2.0 g, 30 mmol). After 2 hours, the reaction mixture was cooled to room temperature and propionic acid was evaporated. The obtained crude product was subjected to silica-gel column using methanol: chloroform (2:98 v/v) as an eluent to yield purple crystalline solid of 5,10,15,20-Tetrakis(3',4'-dimethoxyphenyl)porphyrin (**I)** (14%) (**Figure S1**). The formation of **I** was confirmed from ^{1}H NMR and ESI–MS (**Figure S2 and S3**).

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): -2.75 (2H, s), 3.9 (12H, s), 4.18 (12H, s), 7.26-7.25 (4H), 7.78-7.75 (8H, m), 8.90 (8H, s).

ESI–MS calculated for $C_{52}H_{46}N_4O_8$: 854,94; found: 855.34.

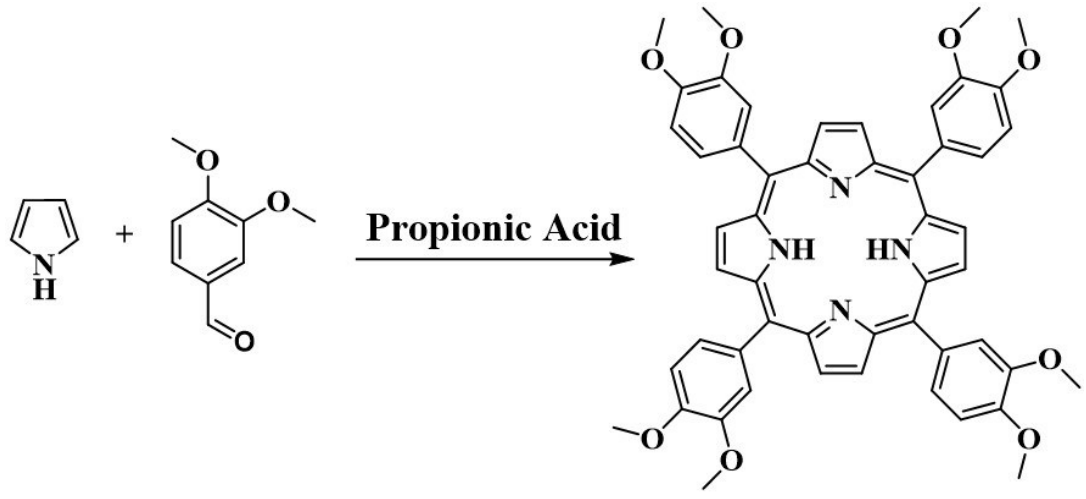

Figure S1. Synthetic protocol for 5,10,15,20-Tetrakis(3',4'-dimethoxyphenyl) porphyrin.

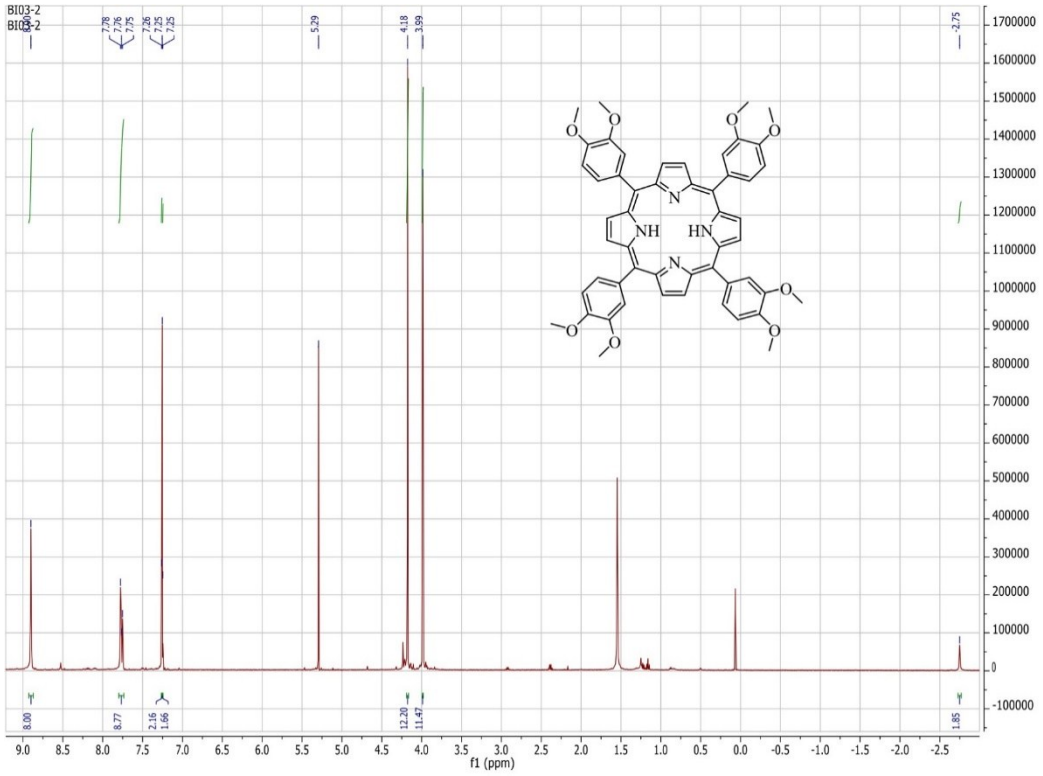

Figure S2. [1]H-NMR spectra of 5,10,15,20-Tetrakis(3',4'-dimethoxyphenyl) porphyrin.

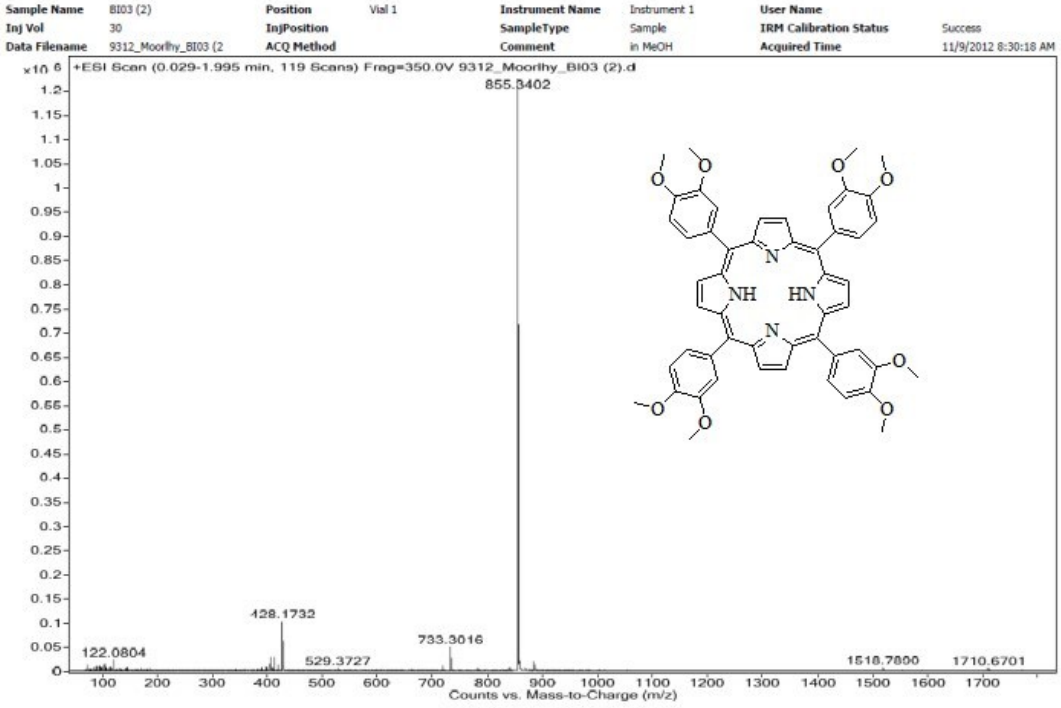

Figure S3. ESI-MS of 5,10,15,20-tetrakis(3',4'-dimethoxyphenyl)porphyrin.

Synthesis of 5,10,15,20-Tetrakis(3',4'-dihydroxyphenyl) porphyrin: 2.4 g of **I** (2.8 mmol) from the previous step was dissolved in dry CH_2Cl_2 (100 ml) under argon atmosphere, followed by dropwise addition of 22 mL of 1M BBr_2 in CH_2Cl_2 at -78°C. After 24 hours, 50 mL of water was added and extracted with ethyl acetate: methanol (97:3) solvent mixture. The organic layer was collected dried over anhydrous sodium sulphate. The solution was reduced to a small volume on a rotary evaporator. The residue was then chromatographed on a dry silica gel column using ethyl acetate-MeOH (9:1, v/v) as the eluent to give 5,10,15,20-tetra(3',4'-dihydroxyphenyl)porphyrin **(II)** (71%) (**Figure S4**). The compound formation was confirmed by ^{1}H NMR (**Figure S5)** and ESI-MS (**Figure S6**).

^{1}H NMR (500 MHz, CH_3OD, δ ppm): 7.51-7.49 (4H, d, J=10, phenyl), 7.99-7.98 (4H, d, J=5, phenyl), 8.16 (4H, s, phenyl), 8.82 (8H, s, pyrrole).

ESI–MS calculated for $C_{44}H_{30}N_4O_8$: 742.73; found 743.2.

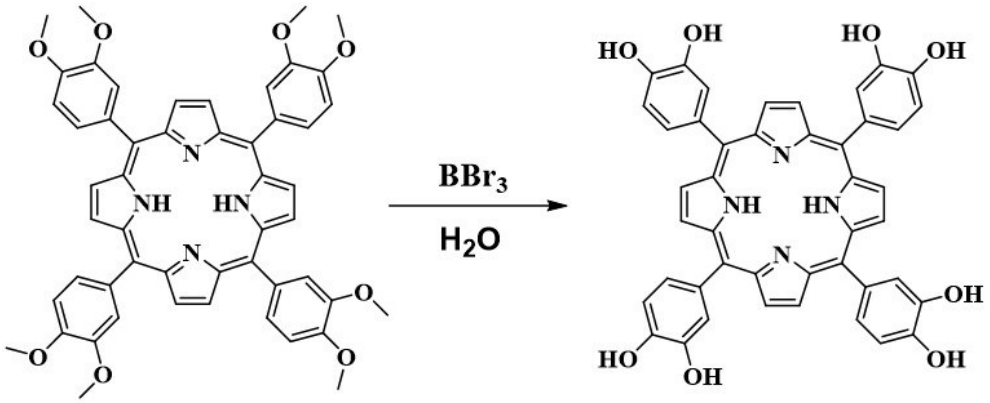

Figure S4. Synthetic protocol for 5,10,15,20-tetrakis(3',4'-dihydroxyphenyl)porphyrin.

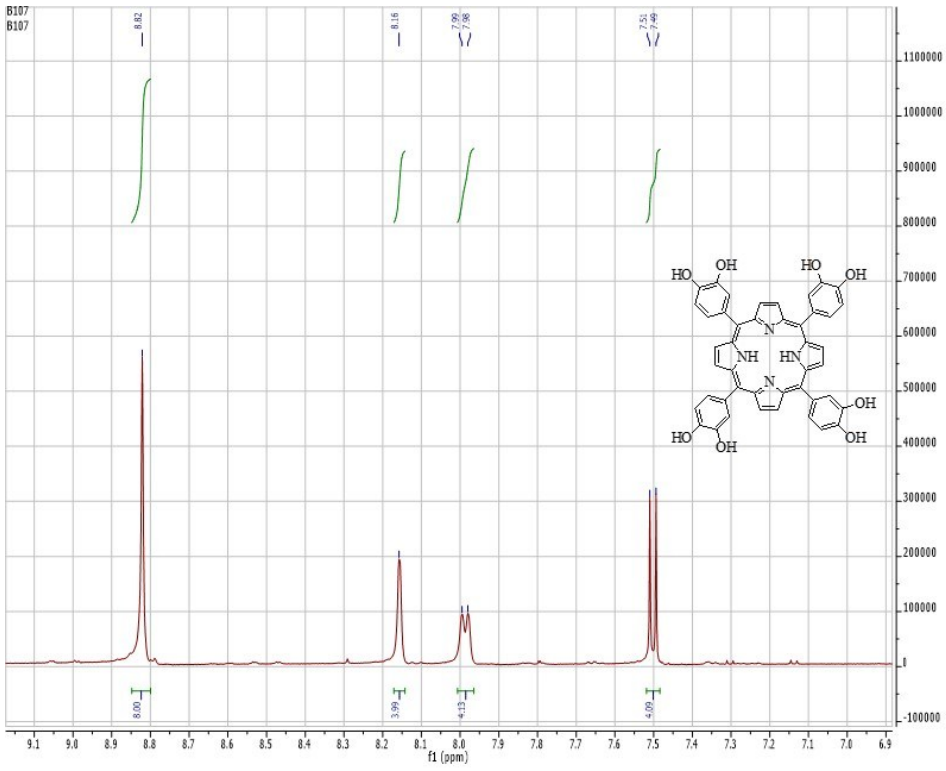

Figure S5. [1]H-NMR spectra of 5,10,15,20-tetrakis(3',4'-dihydroxyphenyl)porphyrin.

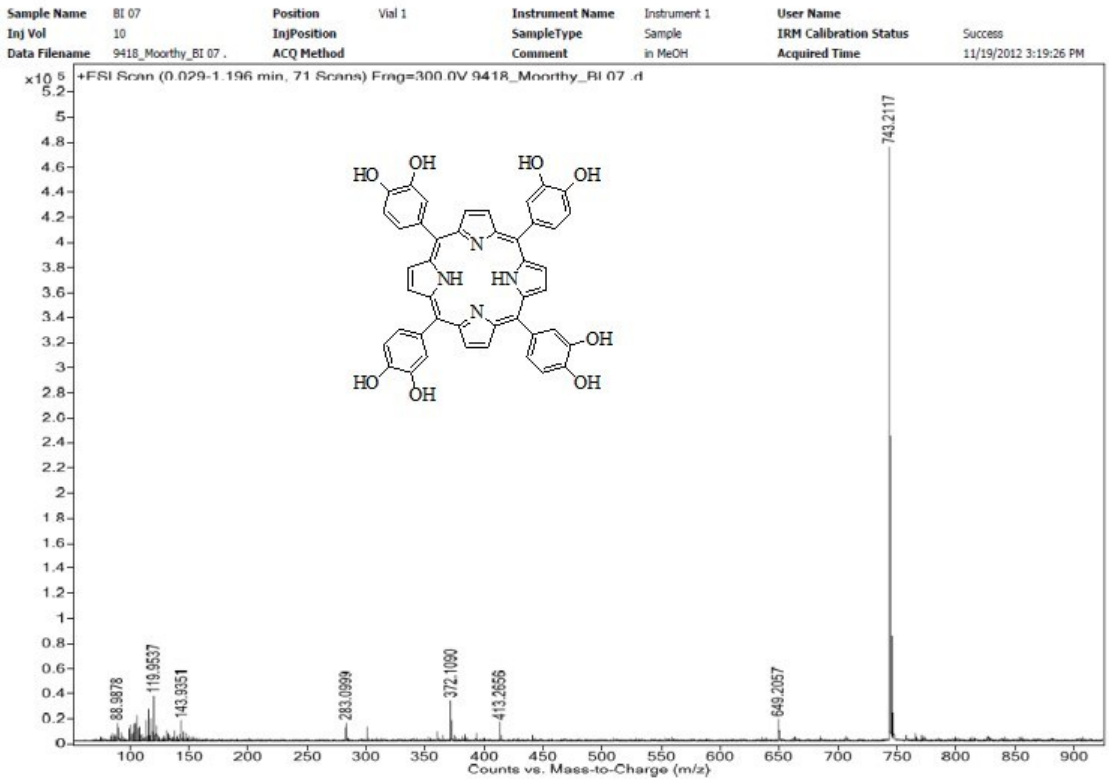

Figure S6. ESI-MS of 5,10,15,20-tetrakis(3',4'-dihydroxyphenyl)porphyrin.

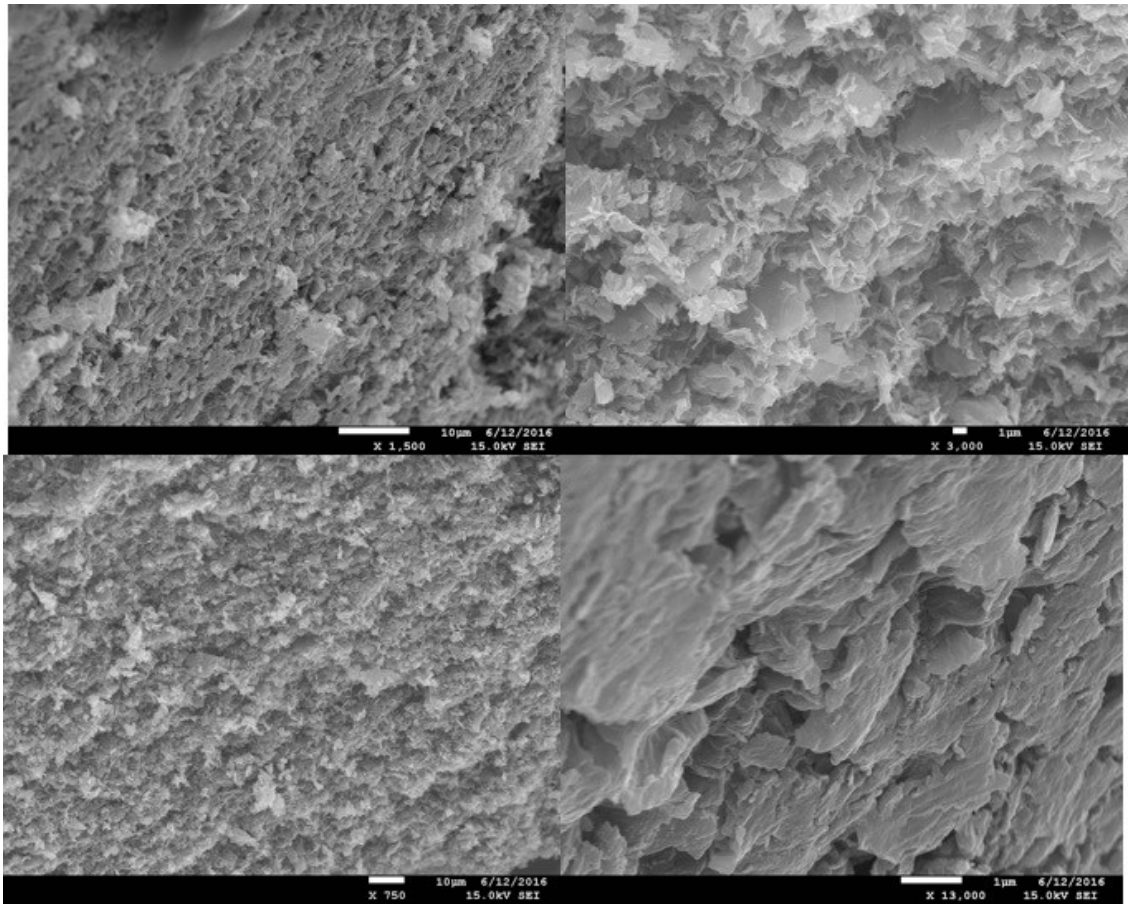

Figure S7. FESEM images of *Por*-GOF displaying stacked sheets. Images were obtained from the same sample at different locations.

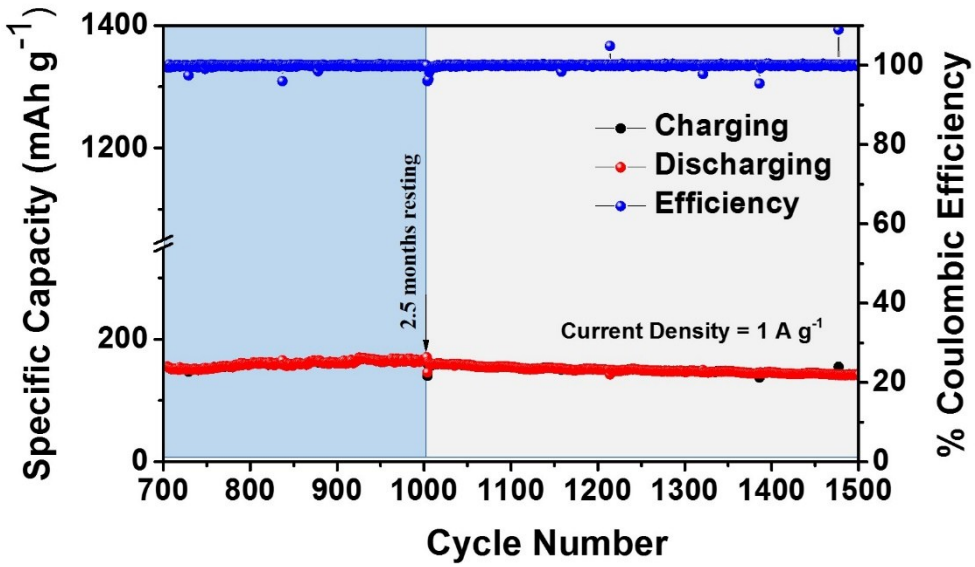

Figure S8. Cycling stability of *Por*-GOF tested after a 2.5 month resting.

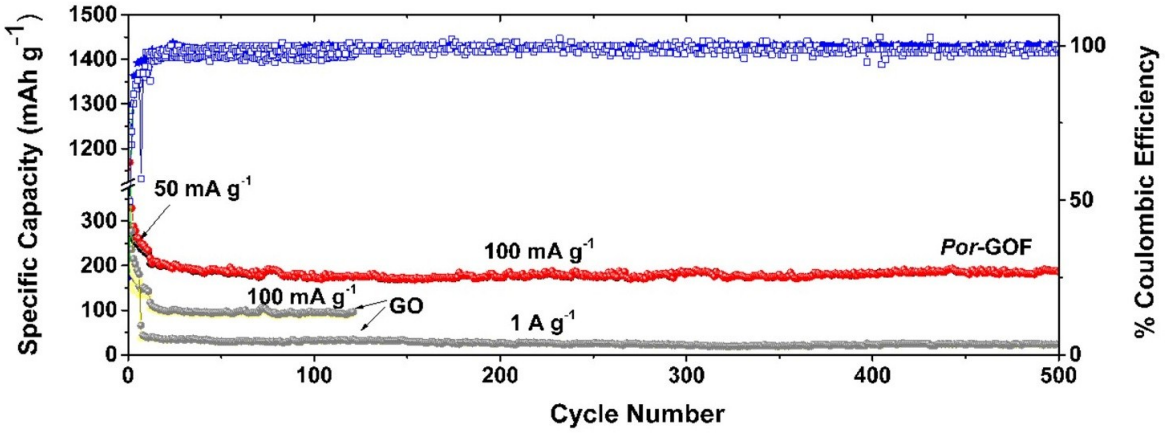

Figure S9. Cycling stability of *Por*-GOF at a current density of 100 mA g^{-1}, GO at a current density of 100 mA g^{-1} and 1 A g^{-1} respectively.

Table S1. Comparison of carbon-based anodes in sodium-ion batteries

Material	Synthesis method	Potential Range (V)	Electrolyte	Capacity (mA h g^{-1})	Cycling stability	Rate capability	Remarks	Studies performed after prolonged resting	Ref.
Por-GOF	Reducing and pillaring of GO using porphyrin molecule	0.005 – 3	$NaClO_4$ in EC, PC and FEC	268 at 50 mA g^{-1}	~200 mAhg^{-1} obtained after 500 cycles at 0.1 A g^{-1}	204 mA h g^{-1} at 0.1 A g^{-1} 196 mA h g^{-1} at 0.2 A g^{-1}	Highly stable cycling performance. ~100 % capacity retention even after 720 hours of resting period.	Yes	This work
Reduced graphene oxide	Heat treatment of GO under N_2 atmosphere	0.01 - 2	$NaClO_4$ in PC	174.3 at 40 mA g^{-1}	~141 mA h g^{-1} at 0.04 A g^{-1} after 1000 cycles was obtained.	150.9 mA h g^{-1} at 0.2 A g^{-1} 118.7 mA h g^{-1} at 0.4 A g^{-1}	A slower capacity decay at higher current density was observed.	No	[1]
Crumpled graphene paper	Thermal annealing at 600°C in Ar atmosphere	0.001 - 2.5	$NaClO_4$ in PC	183 at 100 mA g^{-1}	~100 mA h g^{-1} capacity at 0.1 A g^{-1} was observed after 500 cycles	ca.100 mA h g^{-1} at 4 A g^{-1} 61 mA h g^{-1} at 8 A g^{-1}	A specific capacity of less than 150 mA h g^{-1} was observed when cycled at 1 A g^{-1}.	No	[2]
Reduced graphene oxide	Thermal annealing under dynamic vacuum	0.1-2.5	$NaPF_6$ in DMC and DC	248 at 100 mA g^{-1}	~248 at 0.1 A g^{-1} was obtained in the 50th cycle	220 mA h g^{-1} at 1 A g^{-1} 175 mA h g^{-1} at 5 A g^{-1}	26% degradation in capacity was observed in the 5th cycle.	No	[3]

Reduced graphene oxide	$SnCl_2$ based GO reduction	0.005 - 3	$NaClO_4$ in EC, PC and FEC	272 at 50 mA g^{-1}	~120 at 0.05 A g^{-1} was obtained in the 300th cycle	146 mA h g^{-1} at 0.1 A g^{-1} 109 mA h g^{-1} at 0.2 A g^{-1}	A slow capacity decay could be observed in the later cycles.	No	[4]
Expanded graphitic materials	Heat treatment of GO in nitrogen atmosphere.	0.003 - 2	$NaPF_6$ in EC and DC	203 at 37.2 mA g^{-1}	~150 mA h g^{-1} retained after 50 cycles at 0.0372 A g^{-1}.	~200 mA h g^{-1} at 0.0186 A g^{-1} ~100 mA h g^{-1} at 0.372 A g^{-1}	Modest performance was observed at high current densities. .	No	[5]
Single layered graphene	Chemical vapour deposition onto copper foil	0 - 2.8	$NaPF_6$ in EC and DC	21 µA h cm^{-2} at 5 µA cm^{-2}	~14.3 µA h cm^{-2} retained after 100 cycles at 5 µA cm^{-2}.	4.6 µA h cm^{-2} at 50 µA cm^{-2}	Evaluated as an unsuitable electrode for sodium storage..	No	[6]
Graphene nanosheets	GO reduced by heating at 300ºC in Argon atmosphere	0.4 - 2	$NaClO_4$ in EC and DC	220 at 30mA g^{-1}	Slightly less than 200 mA h g^{-1} after 300 cycles at 0.03 A g^{-1}.	~105 mA h g^{-1} at 5 A g^{-1} ~73 mA h g^{-1} at 10 A g^{-1}	Around 80% of the capacity can be retained after 300 cycles.	No	[7]
Graphene nanosheets	Microplasma assisted synthesis	0.01 – 2	$NaClO_4$ in EC and DC	250 at 30 mA g^{-1}	Slightly less than 150 mA h g^{-1} after 500 cycles at 0.1 A g^{-1}	~150 mA h g^{-1} at 1 A g^{-1} ~110 mA h g^{-1} at 5 A g^{-1}	Graphene sheets with higher oxygen functional groups can lead to higher capacity loss with only 75 % of capacity retention.	No	[8]
Porous graphene sheet	Ferric nitrate used to create pores on GO	0.01 – 3	$NaClO_4$ in EC and DC	193 at 50 mA g^{-1}	~195 mA h g^{-1} retained after 50 cycles at 0.05 A g^{-1}.	~111 mA h g^{-1} at 1 A g^{-1}	Stable cycling for more than 10000 cycles.	No	[9]
Reduced	Thermal annealing	0.01 –	NA	140 at 100	~100 mA h g^{-1}	~200 mA h g^{-1} at	A slow capacity	No	[10]

graphene oxide	in Ar atmosphere	2.5		mA g^{-1}	retained after 1000 cycles at 0.1 A g^{-1}.	0.02 A g^{-1} ~150 mA h g^{-1} at 0.04 A g^{-1}	decay could be observed in the later cycles.		
Expanded graphite	Heat treatment based reduction of GO	0 -2	$NaClO_4$ in PC	280 at 20 mA g^{-1}	Slightly less than 300 mA h g^{-1} after 30 cycles at 0.02 A g^{-1}	~184 mA h g^{-1} at 0.1 A g^{-1} ~91 mA h g^{-1} at 0.2 A g^{-1}	Retains 73.92% of its capacity after 2,000 cycles.	No	11
Few layered graphene	Chemical vapour deposition	0.01 - 2	$NaPF_6$ in diglyme	150 at 200 mA g^{-1}	Slightly less than 120 mA h g^{-1} after 8000 cycles at 12 A g^{-1}	~125 mA h g^{-1} at 10 A g^{-1} ~100 mA h g^{-1} at 30 A g^{-1}	Ether-based electrolyte used as a non-stick coating to facilitate sodium storage.	No	12

(PC = propylene carbonate, FEC = fluoroethylene carbonate, DMC = dimethyl carbonate, EC = ethylene carbonate, DC = diethyl carbonate)

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