Supplementary information

Single Source Precursor-based Solvothermal Synthesis of Heteroatom-doped Graphene and Its Energy Storage and Conversion Applications

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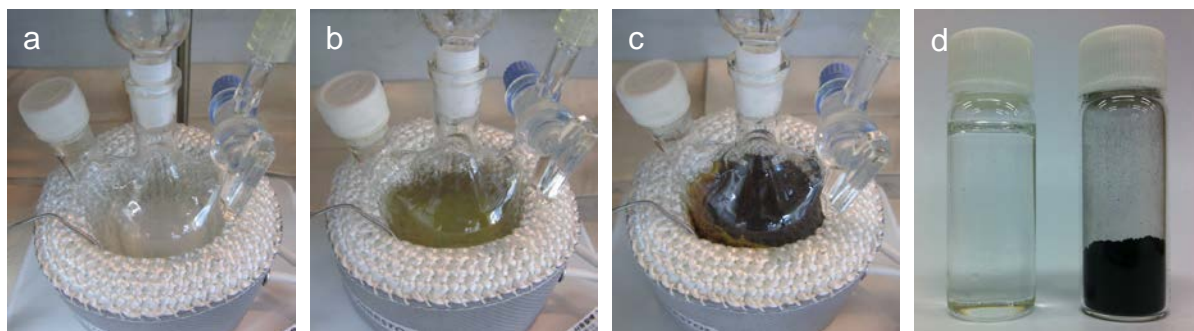
Supplementary Figure S1: Photographs of synthesis of the S-doped graphene. (a) A mixture of DMSO and NaOH in a reactor (room temperature). (b) The mixture started to boil at ~250 °C, and (c) the mixture was boiling about 1 h. (d) 10 ml of DMSO and 0.35 g of the S-doped graphene.
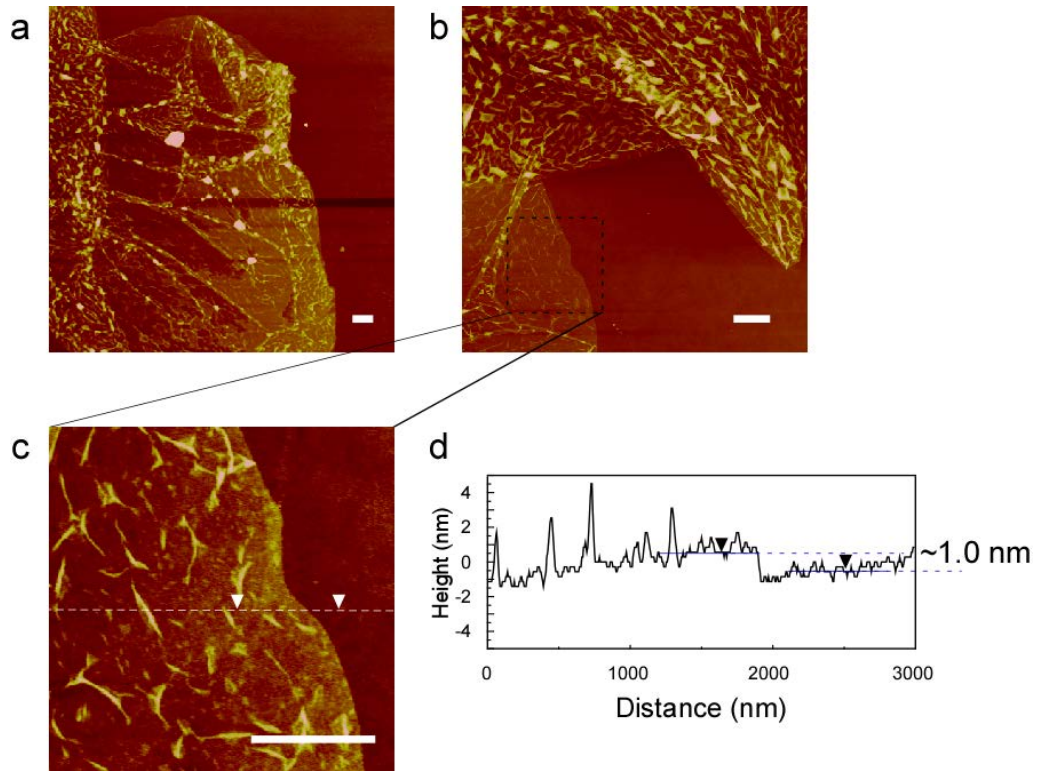
Supplementary Figure S2: AFM images of the S-doped graphene. (a, b, and c) AFM images of the S-doped graphene with different magnifications (All the scale bars are 1000 nm.) (d) Height profile of the S-doped graphene.
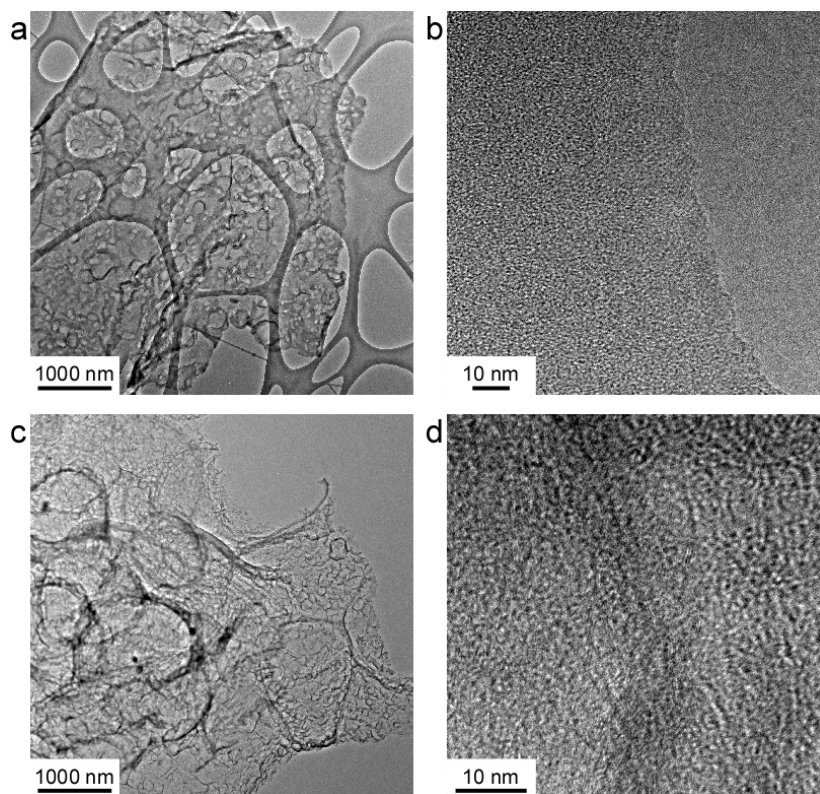
Supplementary Figure S3: TEM and high-resolution TEM images of the N-doped graphene and pristine solvothermal graphene. (a, b) TEM and HR- TEM images of the N-doped graphene. (c, d) TEM and HR-TEM images of the pristine solvothermal graphene.
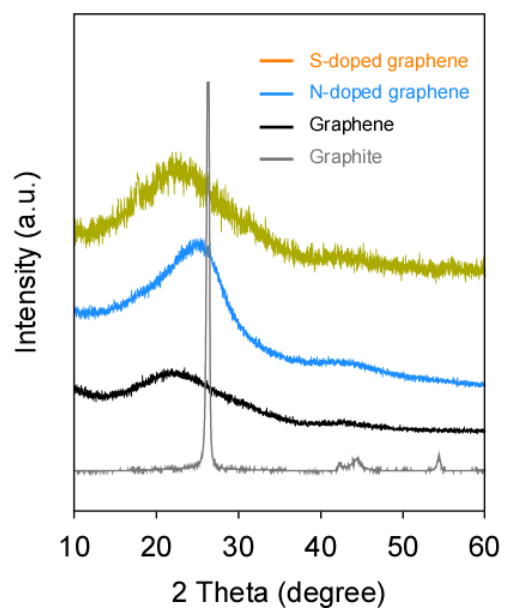
Supplementary Figure S4: XRD patterns of the S-doped graphene, N-doped graphene, pristine solvothermal graphene, and graphite.

Bulk conductivity

Bulk conductivity of the S-doped graphene, N-doped graphene and pristine solvothermal graphene were measured according to a literature procedure[1]. The samples were filled into a channel; two sides of the channel are used as electrodes. The conductivity of samples was measured using the equation: $\sigma = R \cdot L / A$

Where:

σ is the conductivity, Sm^{-1}

R is the resistance, Ω

L is the distance between the two electrodes, m

A is the cross-section area of the sample, m^2

Sample	Conductivity ($S\ m^{-1}$)
S-doped graphene	0.607×10^{-3}
N-doped graphene	0.416×10^{-3}
Pristine graphene	0.121
Pristine graphene[20]	0.067

20   Choucair, M., Thordarson, P. & Stride, J. A. Gram-scale production of graphene based on solvothermal synthesis and sonication. *Nat. Nanotechnol.* **4**, 30-33 (2009).
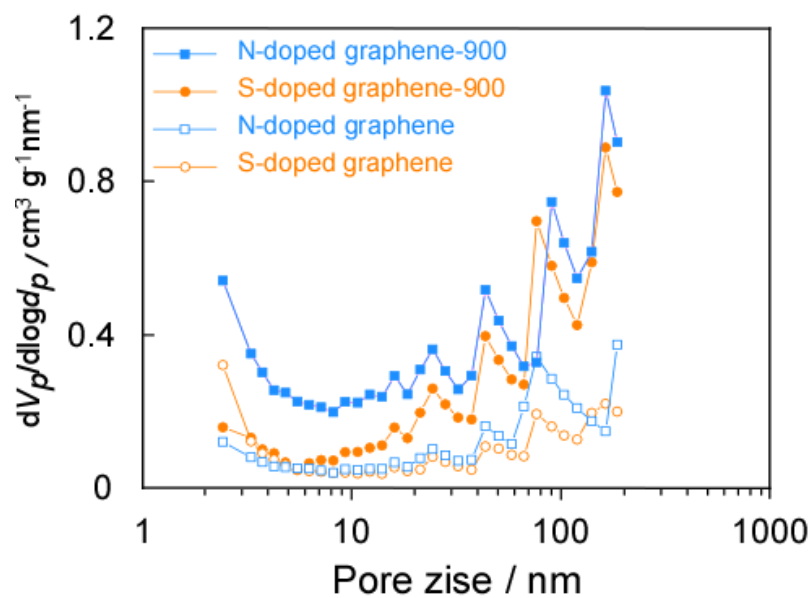
Supplementary Figure S5: Pore size analysis. Pore distributions of the S-doped graphene, N-doped graphene, S-doped graphene-900 (annealing at 900 °C), and N-doped graphene-900 (annealing at 900 °C).

Supplementary Table S1: Elemental analysis data of the S-doped graphene, N-doped graphene and pristine solvothermal graphene.

Sample	% Composition/Mass				
	C	H	N	S	O
S-doped graphene	70.13	1.49	0.08	22.83	5.47
N-doped graphene	65.41	2.40	12.25	-	19.94
Pristine graphene	88.41	0.99	0.09	-	10.51
Pristine graphene[20]	78.49	2.69	-	-	18.82

A previous study demonstrated that most of the oxygen present in solvothermal graphene was adsorbed water[20].
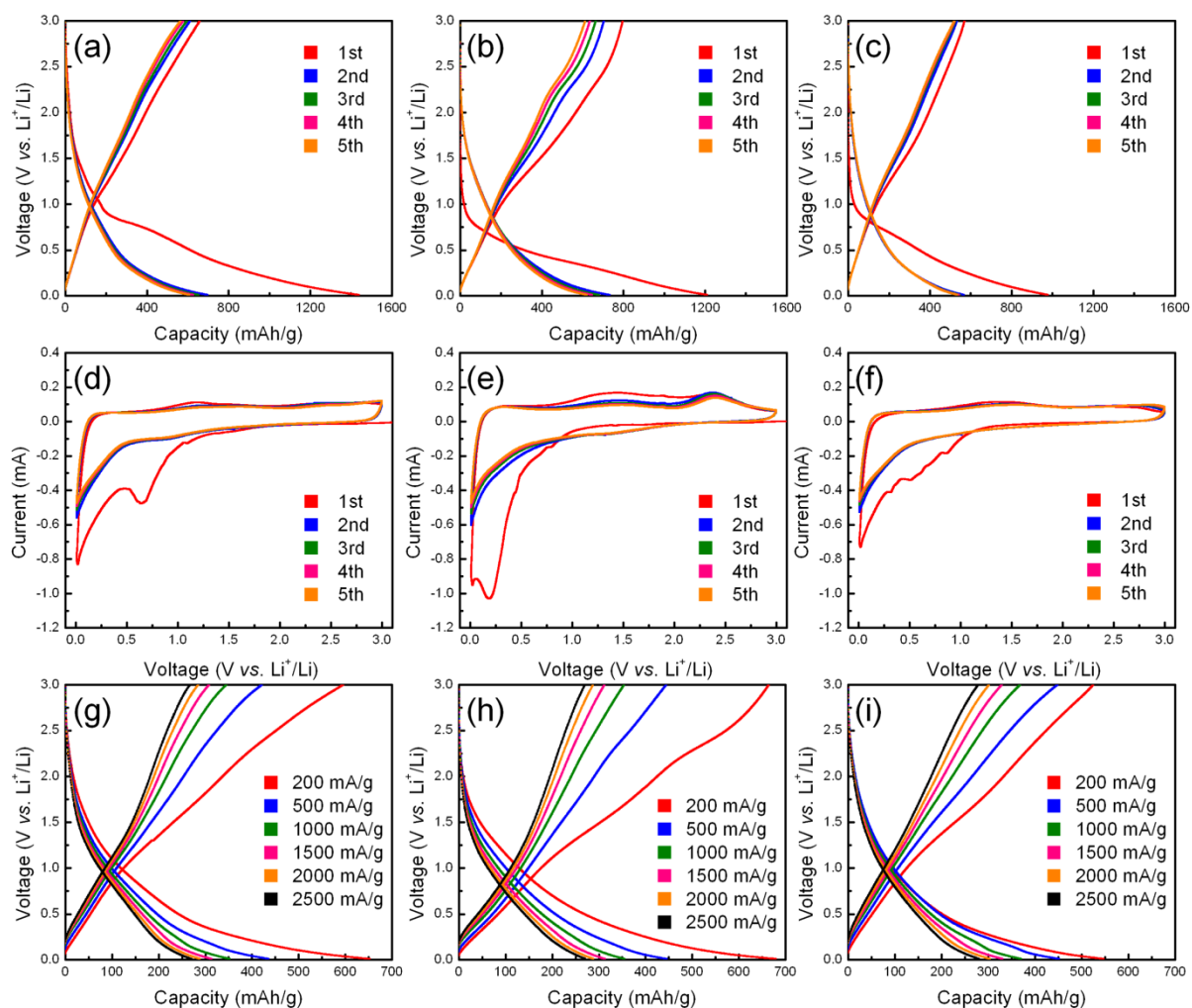
Supplementary Figure S6: Galvanostatic charge and discharge profiles of (a) the pristine solvothermal graphene, (b) S-doped graphene and (c) N-doped graphene electrodes at a current density of 200 mA g^{-1} for initial 5 cycles. Cyclic voltammograms of (d) the pristine solvothermal graphene, (e) S-doped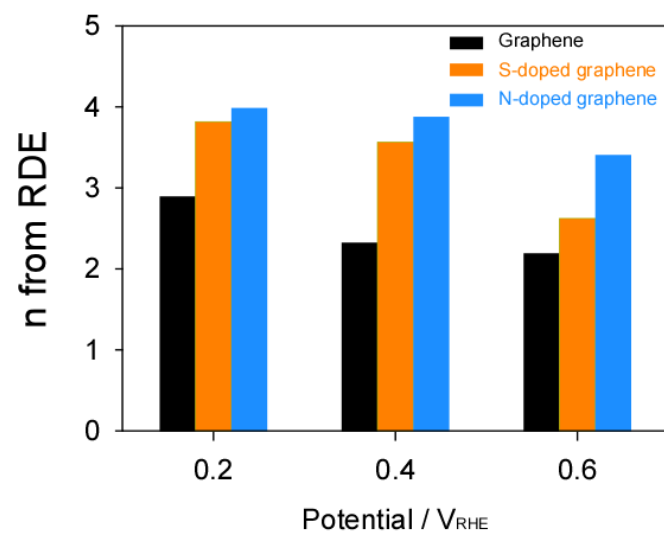 graphene and (f) N-doped graphene electrodes at a scanning rate of 0.1 mV s^{-1}. Galvanostatic charge and discharge profiles of (g) the pristine solvothermal graphene, (h) S-doped graphene and (i) N-doped graphene electrodes at various current rates.

Supplementary Table S2: Reversible capacities of graphene as anode materials.

sample	Current density	Voltage range (vs. Li+/Li)	Initial reversible capacity	Reversible capacity after cycles	Ref.
GO annealed at 600 ℃	50 mAh g^{-1}	0.005 – 3.0 V	794 mAh g^{-1}	~700 mAh g^{-1} (15th cycle)	30
GO annealed at 300 ℃	50 mAh g^{-1}	0.005 – 3.0 V	1013 mAh g^{-1}	834 mAh g^{-1} (15th cycle)	30
Electron beam reduced GO	50 mAh g^{-1}	0.005 – 3.0 V	1054 mAh g^{-1}	784 mAh g^{-1} (15th cycle)	30
Hydrazine reduced GO	50 mAh g^{-1}	0.005 – 3.0 V	330 mAh g^{-1}	~200 mAh g^{-1} (15th cycle)	30
GO annealed at 1050 ℃	100 mAh g^{-1}	0.01 – 3.0 V	~400 mAh g^{-1}	~270 mAh g^{-1} (100th cycle)	26
GO annealed at 1050 ℃ + Heat treatment in NH$_3$ (N-doped graphene)	100 mAh g^{-1}	0.01 – 3.0 V	~500 mAh g^{-1}	~360 mAh g^{-1} (17th cycle), ~450 mAh g^{-1} (100th cycle), ~680 mAh g^{-1} (500th cycle)	26
GO annealed at 1000 ℃ with triphenylmethane	100 mAh g^{-1}	0.01 – 3.0 V	280 mAh g^{-1}	~280 mAh g^{-1} (80th cycle)	14
GO annealed at 1000 ℃ with triphenylphosphine (P-doped graphene)	100 mAh g^{-1}	0.01 – 3.0 V	460 mAh g^{-1}	~460 mAh g^{-1} (80th cycle)	14
Hydrazine reduced GO	50 mAh g^{-1}	0.01 – 3.5 V	540 mAh g^{-1}	290 mAh g^{-1} (20th cycle)	31
GO annealed at 500 ℃	50 mAh g^{-1}	0.01 – 3.0 V	955 mAh g^{-1}	638 mAh g^{-1} (30th cycle)	32
GO annealed at 600 ℃ in NH$_3$ (N-doped graphene)	50 mAh g^{-1}	0.01 – 3.0 V	1043 mAh g^{-1}	873 mAh g^{-1} (30th cycle)	32
GO annealed at 800 ℃ in BCl$_3$ (B-doped graphene)	50 mAh g^{-1}	0.01 – 3.0 V	1549 mAh g^{-1}	1227 mAh g^{-1} (30th cycle)	32
Solvothermal synthesis using methanol (Pristine graphene)	200 mAh g^{-1}	0.01 – 3.0 V	660 mAh g^{-1}	577 mAh g^{-1} (150th cycle)	this work
Solvothermal synthesis using DMF (N-doped graphene)	200 mAh g^{-1}	0.01 – 3.0 V	797 mAh g^{-1}	479 mAh g^{-1} (150th cycle)	this work
Solvothermal synthesis using DMSO (S-doped graphene)	200 mAh g^{-1}	0.01 – 3.0 V	570 mAh g^{-1}	491 mAh g^{-1} (150th cycle)	this work

14   Zhang, C., Mahmood, N., Yin, H., Liu, F. & Hou, Y. Synthesis of Phosphorus-Doped

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Supplementary Figure S7: Potential dependent electron transfer number of the pristine solvothermal graphene, N-doped graphene and S-doped graphene.