Electronic Supplementary Information

Nitrogen-doped graphene as a cathode material for dyesensitized solar cells: effects of hydrothermal reaction and annealing on electrocatalytic performance

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Fig. S1 Chemical formula of the used sensitizer: 3-[6-[4-[4'-dihexyloxybiphenyl-4-yl-amino-] phenyl [-4,4'-dihexylcyclopenta-[2,1-b:3,4-b]dithiphene-2-yl]-2-cyanoacrylic acid.



Fig. S2 Precusors of graphene oxide/urea dispersion with and without H_2SO_4 flocculation for hydrothermal reaction.



Fig. S3 Impedance spectra for symmetric dummy cells fabricated with NG-12S





Fig. S4 Nyquist plots in the high-frequency region for the symmetric dummy cells with nitrogen doped graphene electrodes annealed at 80 $^{\circ}$ C (a) and 350 $^{\circ}$ C(b), respectively. Bias voltages were given as 0, 0.2, 0.4, 0.6, 0.8 V. Insets in graphs (a

and b) indicate the Nyquist plots over the whole frequency range of from 200 kHz to 200 mHz.

 Table S1 Fitting results of XPS data of nitrogen doped graphene nanosheets without

 annealing^a

N peaks /at%	B.E./ eV	NG-2	NG-6	NG-12	NG-18
N1	398.5	3.17	2.94	3.39	2.24
N2	399.8	3.25	3.57	3.35	3.11
N3	401.1	0.41	0.57	0.36	1.03
N4	402.8	0.49	0.28	0.53	0.34
O peaks /at%	B.E./ eV				
01	530.9	3.92	3.72	4.31	4.94
02	532.0	4.81	2.14	1.12	4.90
03	533.5	1.90	3.83	3.66	2.66
C peaks /%	B.E./ eV				
C1	284.6	41.4	42.4	46.9	43.5
C2	285.3	11.6	15.1	9.38	10.2
C3	286.2	12.1	12.1	13.8	12.7
C4	287.8	4.63	3.44	5.13	6.21
C5	289.2	11.5	9.88	8.08	5.72

^{*a*} NG-2, NG-6, NG-12, and NG-18 mark the cathodes based on NG hydrothermally prepared for 2, 6, 12, and 18 hrs, respectively. **N1**: pyridinic N (398.5 eV), **N2**: pyrrolic N (399.8 eV), **N3**: quaternary N (401.1 eV), and **N4**: N-oxides of pyridinic N (402.8 eV); **O1**: C-O (530.9 eV), **O2**: C=O (532.0 eV), and **O3**: O-C=O (533.5 eV); **C1**: C=C (284.6 eV), **C2**: C=N (285.3 eV), **C3**: C – O& C–N (286.2 eV), **C4**: C=O (287.8 eV), and **C5**: O-C=O (289.2 eV).

N peaks /at%	B.E./ eV	NG-2S	NG-6S	NG-12S	NG-18S
N1	398.5	1.40	1.70	2.52	2.10
N2	399.8	2.61	2.80	4.06	3.17
N3	401.1	0.32	0.43	0.59	0.69
N4	402.8	1.18	1.10	0.47	0.53
O peaks /at%	B.E./ eV				
01	530.9	3.92	4.32	3.89	3.89
02	532.0	2.27	1.60	1.73	0.64
03	533.5	4.00	3.25	3.22	4.29
C peaks /%	B.E./ eV				
C1	284.6	44.9	47.0	44.7	48.9
C2	285.3	12.3	13.1	15.8	10.5
C3	286.2	13.4	11.3	10.8	11.9
C4	287.8	4.29	3.99	4.12	5.01
C5	289.2	9.38	9.47	8.16	8.33

 Table S3 Fitting results of XPS data of nitrogen doped graphene nanosheets after

 annealing^a

^{*a*}NG-2S, NG-6S, NG-12S, and NG-18S represent the annealed cathodes based on the NG prepared hydrothermally for 2, 6, 12, and 18 hrs, respectively. **N1**: pyridinic N (398.5 eV), **N2**: pyrrolic N (399.8 eV), **N3**: quaternary N (401.1 eV), and **N4**: N-oxides of pyridinic N (402.8 eV); **O1**: C-O (530.9 eV), **O2**: C=O (532.0 eV), and **O3**: O-C=O (533.5 eV);. **C1**: C=C (284.6 eV), **C2**: C=N (285.3 eV), **C3**: C – O & C–N (286.2 eV), **C4**: C=O (287.8 eV), and **C5**: O-C=O (289.2 eV).



Fig. S5 Equivalent circuit for fitting the impedance spectra of the DCS based on NG cathode. The used impedance elements are given as follows: R_s is ohmic serial resistance; R_{ct} and $R_{ct,WE}$ are charge transfer resistances at NG sheet/electrolyte interfaces and TiO₂/ electrolyte interfaces; CPE and CPE_{WE} account for constant phase elements of the NG layer and the TiO₂ film; Z_w and Z_{pore} represent Nernst diffusion impedance in the bulk electrolyte and the porous NG layer, respectively.