

Electronic Supplementary Materials

Electropolymerized Supermolecules Derived N, P co-doped Carbon Nanofiber Networks as Highly Efficient Metal-Free Electrocatalyst for Hydrogen Evolution Reaction

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Experiment section

The preparation of PANI-PA supermolecules were achieved by a simple electrochemical polymerization in a three-electrode cell consisting of carbon paper (CP) as both working and count electrode, saturated calomel electrode (SCE) as reference electrode at room temperature. The PANI-PA was electropolymerized onto CP in the electrolyte which was prepared by dissolving 4 mL HCl in 50 mL H₂O and then adding 2.3 g (25 mmol) aniline and 4.71 g phytic acid (5 mmol) to form uniform solution after stirring for half an hour. The constant potential of 0.8 V vs. SCE was applied to the working electrode for 20 min. After that, PANI-PA/CP was washed with water, followed by drying at 80 °C for 6 h and then the pyrolysis is carried out at 800 °C, 900 °C, 1000 °C with a heating rate of 5 °C min⁻¹ for two hours to transform into N,P co-doped carbon nanofiber. The pure PANI was also prepared in the similar way in the absence of phytic acid. The powder sample of PANI-PA-900-P was prepared in the absence of CP according to the published paper.¹

Materials characterization

The morphology was investigated by scanning electron microscope (SEM, Hitachi, S-4800) and transmission electron microscopy (TEM, Tecnai g2 F20). The Raman spectra were recorded at room temperature on a Horiba HR 800 with an argon ion laser operating at 632 nm. X-ray powder diffraction (XRD) was carried out on a Siemens D500 diffractometer with a Cu K α source (1.54056Å). Diffraction data were collected for 2 θ angles from 10° to 90° at a scan rate of 5 ° min⁻¹. The X-ray photoelectron spectroscopy (XPS) analysis was performed on an ESCALAB 250Xi X-ray photoelectron spectrometer using Mg as the excitation source.

Electrochemical measurements

Electrochemical measurements of the samples for HER were carried out using an electrochemical workstation (CHI 760E, CHInstrument, USA) with a typical three-electrode system at the room temperature through both CV and LSV. The scan rate of LSV measurements was 2 mV s^{-1} and the CV stability measurements was taken at the scan rate of 50 mV s^{-1} between -0.4 V - 0 V (V vs. RHE). A carbon rod was used as counter electrode and the obtained samples ($1\text{cm}\times 1\text{cm}$) were used as the working electrode and the SCE as reference electrode. The EIS test of PANI-PA-900 and PANI-900 were performed at a potential of -200 mV using an Autolab electrochemical workstation (Autolab PGSTAT302N, Metrohm-Autolab BV, Netherlands). All potentials were converted to the reversible hydrogen electrode (RHE) to unequivocally compensate for the pH changes. All electrochemical activity data was presented with IR correction.

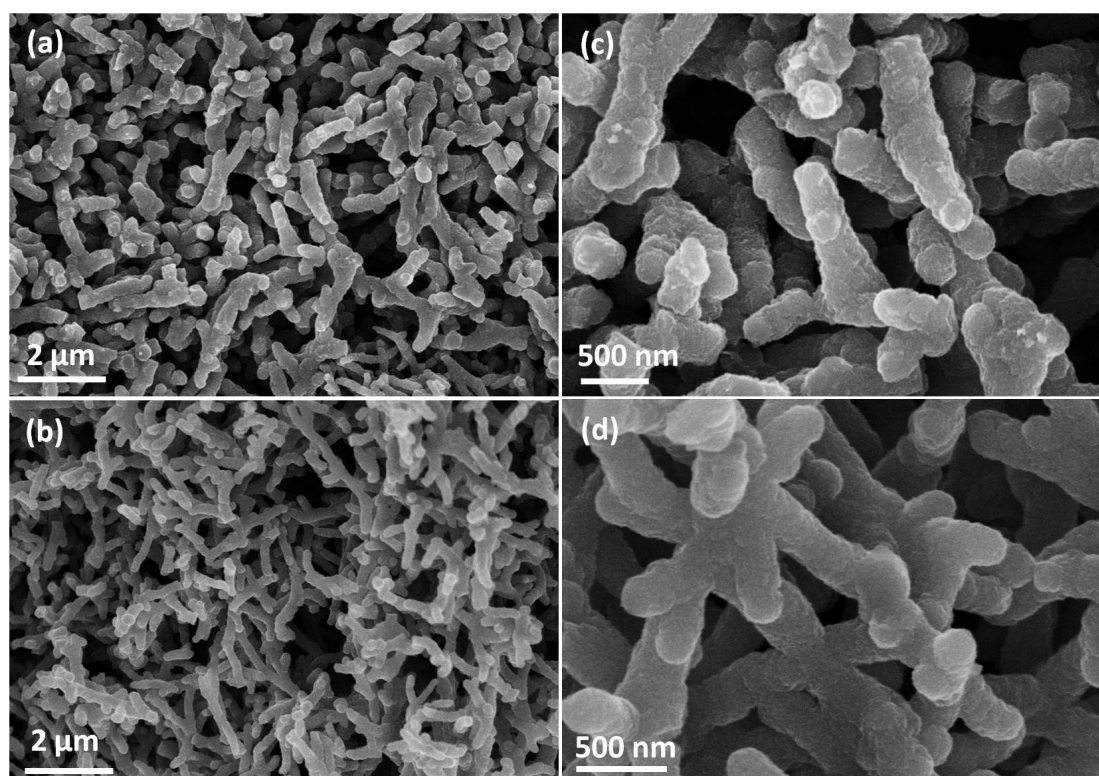


Figure S1. SEM images of (a), (c) PANI and (b), (d) PANI-900.

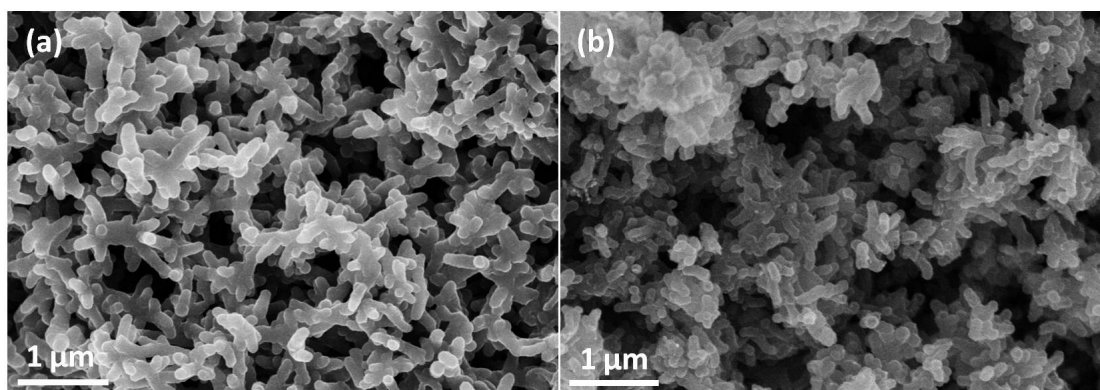


Figure S2. SEM images of (a) PANI-PA and (b) PANI-PA-900.

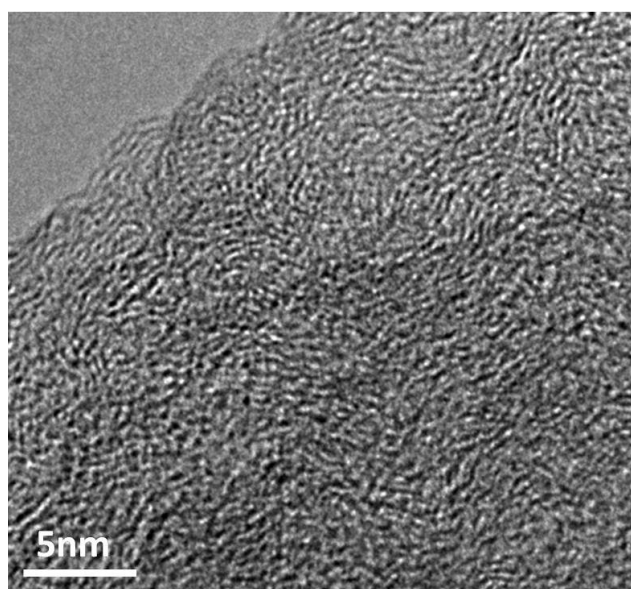


Figure S3. High-resolution TEM image of PANI-PA-900

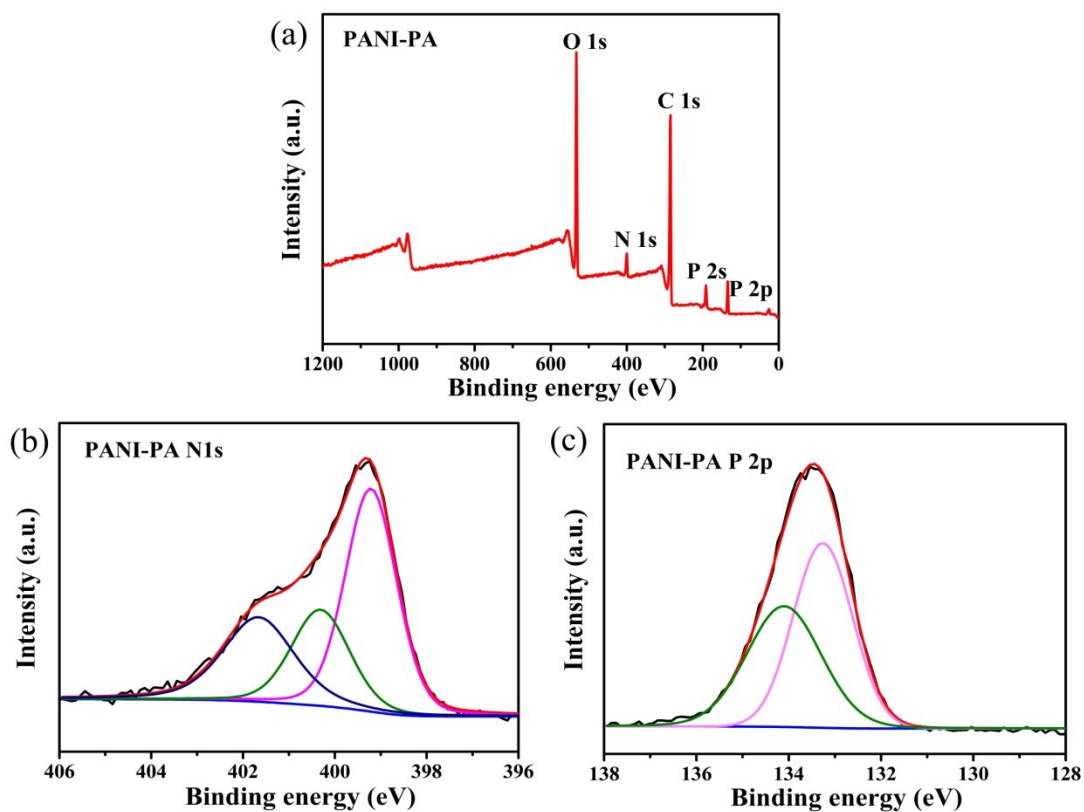


Figure S4. XPS survey spectrum of (a) PANI-PA and (b) N 1s and (c) P 2p spectrum of PANI-PA.

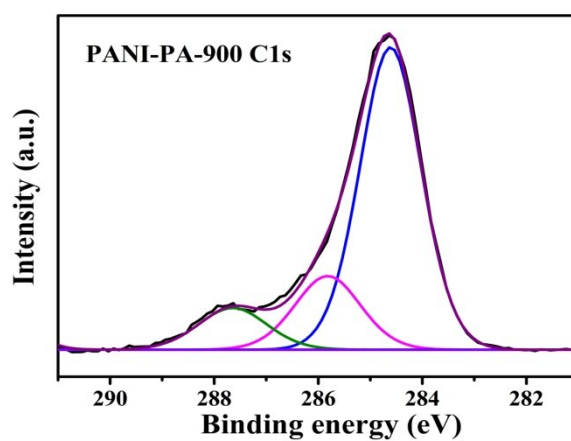


Figure S5. The high resolution C 1s XPS spectra of PANI-PA-900.

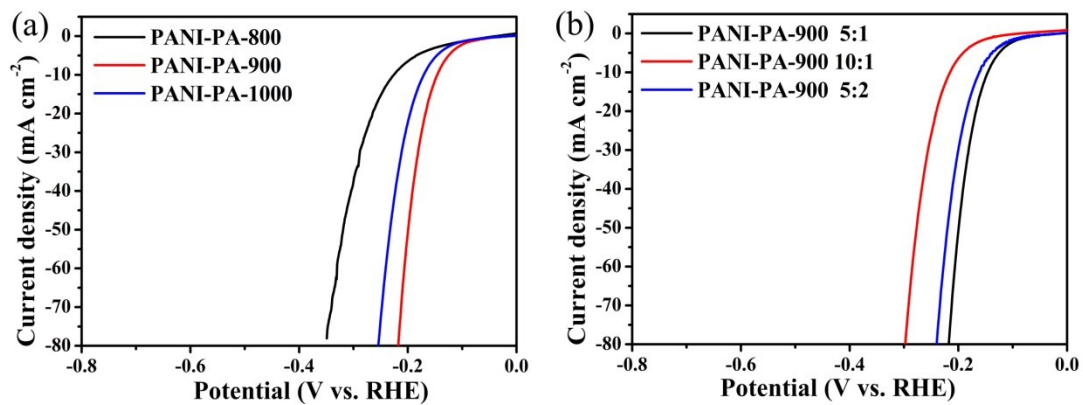


Figure S6. (a) The different pyrolysis temperature at mole ratio of aniline and phytic acid 5:1 and (b) different mole ratio of aniline and phytic acid at 900 °C for HER in 0.5 M H₂SO₄.

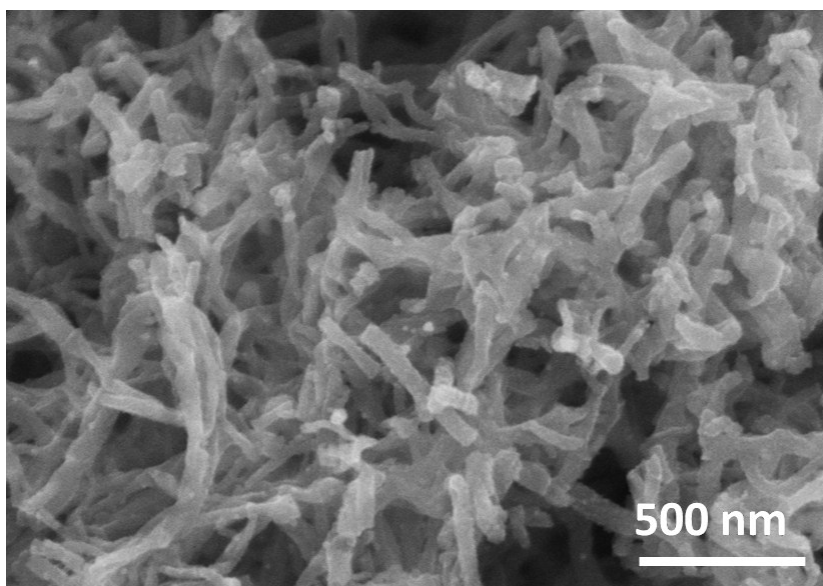


Figure S7. The powder sample of PANI-PA-900 prepared by adding the oxidant.

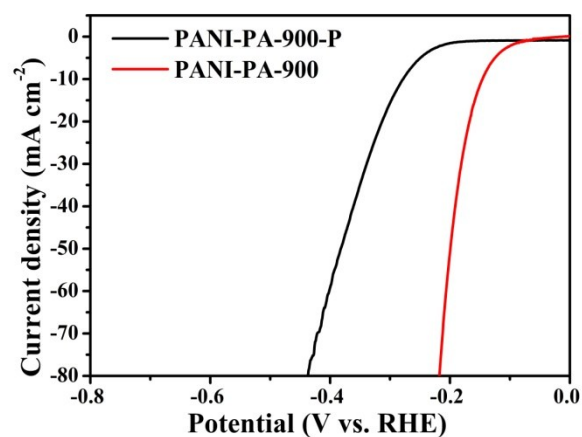


Figure S8. The HER activity of PANI-PA-900-P and PANI-PA-900 in 0.5 M H₂SO₄.

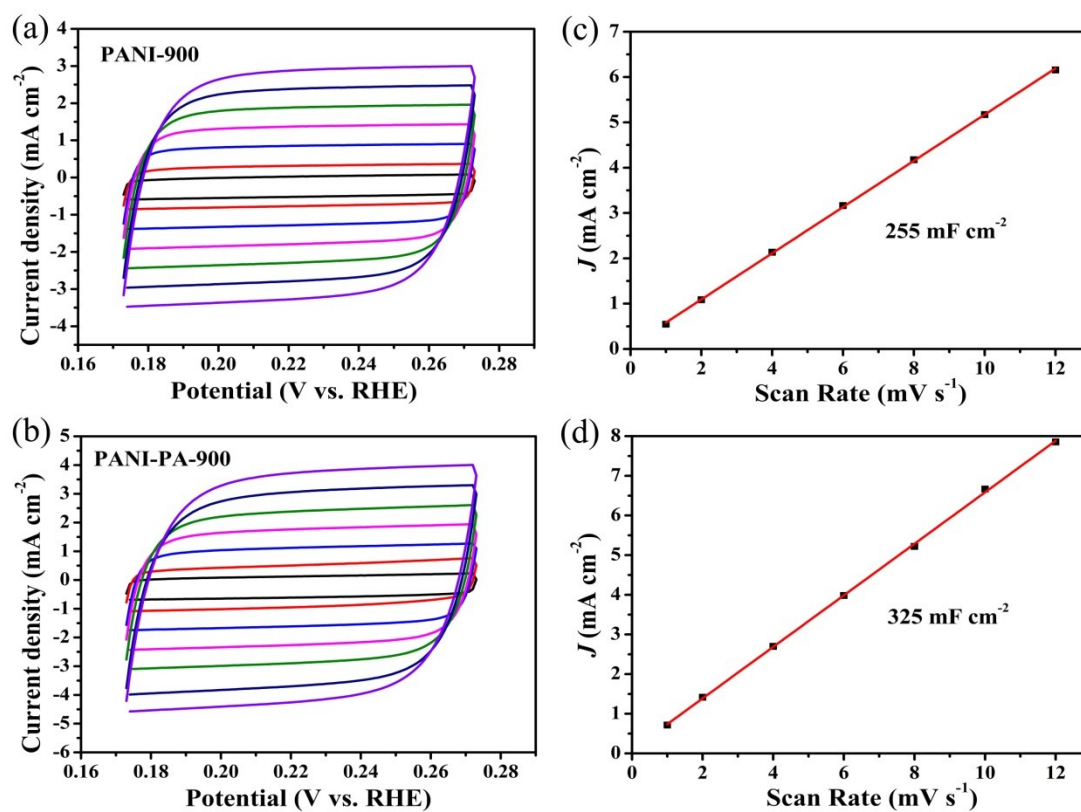


Figure S9. Cyclic voltammetry curves of (a) PANI-900 and (b) PANI-PA-900 in 0.5 H₂SO₄. The capacitive current measured at 0.22 V vs RHE was plotted as a function of scan rate (c) PANI-900 and (d) PANI-PA-900.

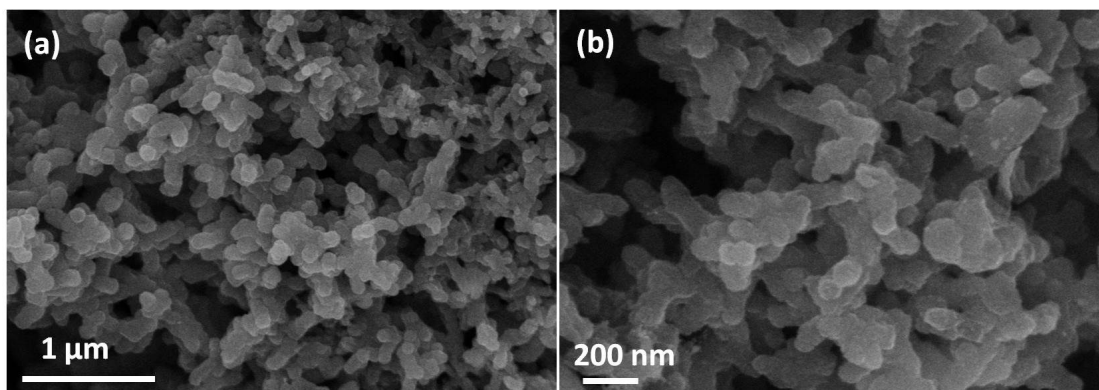


Figure S10. SEM images of PANI-PA-900 after 2000 CV cycles.

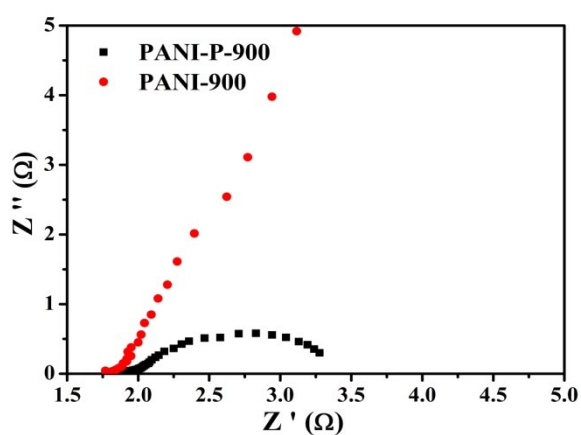


Figure S11. AC impedance spectroscopy of different electrodes at the overpotential of -0.2 V.

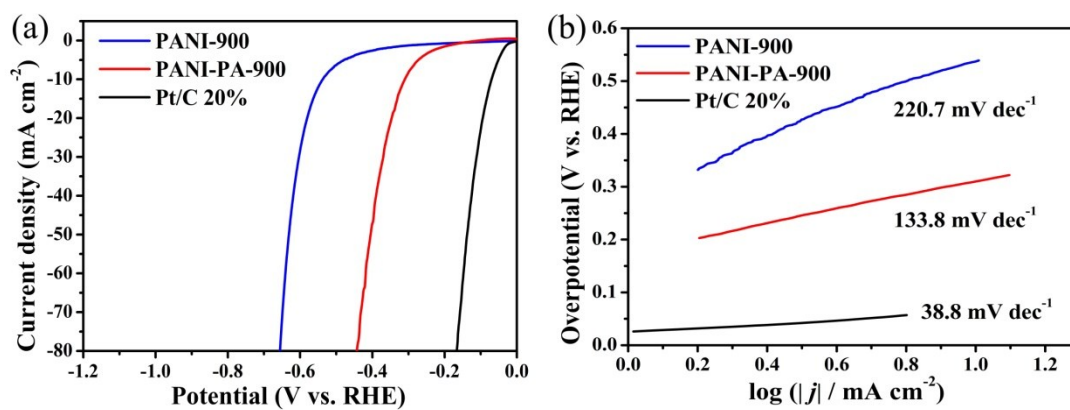


Figure S12. The polarization curves of HER in KOH solution on (a) PANI-900 and PANI-PA-900 and (b) the Tafel plots of different samples.

Table S1. The N and P element compositions in the samples of PANI-PA and PANI-PA-900 by accounting for N, P, and C.

Samples	N content (at%)	P content (at%)
PANI-PA	6.66	7.45
PANI-PA-900	3.27	1.77

Table S2. The comparison of HER performance of PNAI-PA-900 with other metal free electrocatalysts in 0.5 M H₂SO₄.

Catalyst	Onsetpotential (mV)	Overpotential at 10 mA cm ⁻² (mV) 0.5M H ₂ SO ₄	Tafel slope (mV dec ⁻¹)	Ref.
N, P co-doped porous carbon	76	151	69	This work
N,P-Codoped Carbon Networks	60	210 at 30 mV cm ⁻²	89	Angew. Chem. 2016, 128(6): 2270-2274
g-C ₃ N ₄ nanoribbon-G	80	207	54	Angew. Chem. Int. Ed. 2014, 53, 13934–13939.
C ₃ N ₄ @NG	–	240	51.5	Nat. Commun. 2014, 5, 3783.
Nitrogen and phosphorus dual-doped graphene	289	420	91	ACS Nano, 2014, 8 (5), 5290–5296.
Sulfur and nitrogen self-doped carbon	27	116	67.8	Nano Energy (2015) 16, 357–366.
Bacterium derived N, P doped carbon	76	204	58.4	J. Mater. Chem. A, 2015, 3, 7210–7214.
Activated CNT	100	220	73.1	Chem. Commun., 2014, 50, 9340–9342.
C ₃ N ₄ coupled with graphene co-doped by S and Se	92	300	86	J. Mater. Chem. A, 2015, 00, 1-10.
MoP@porous carbon	77	153	66	Angew. Chem. Int. Ed. DOI:10.1002/ange.201604315

Ni ₅ P ₄ -Ni ₂ P nanosheets	54	120	79.1	Angew. Chem. Int. Ed.2015, 54(28): 8188-8192.
Co-C-N complex	-	138	55	J. Am. Chem. Soc. 2015, 137, 15070–15073
Gold@N-Doped Carbon	54.1	130	76.8	Angew.Chem. 2016, 128,8556 –8560
MnO ₂ @PC-RGO	near 0	64	41	Angew. Chem.2015, 127, 13120 –13124

Ref. S1. L. Pan, G. Yu, D. Zhai, H. R. Lee, W. Zhao, N. Liu, H. Wang, B. C.-K. Tee, Y. Shi and Y. Cui, *Proc. Natl Acad. Sci. USA*, 2012, **109**, 9287-9292.