

Supporting Information

Nitrogen and Sulfur-Codoped Porous Carbon Derived from BSA/Ionic Liquid Polymer Complex: Multifunctional Electrode Materials for Water Splitting and Supercapacitor

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Experimental

Chemicals. N-vinyl imidazole (Im, 98%, Sigma-Aldrich) was distilled under vacuum before use and stored in the refrigerator. Bromoacetonitrile, lithium bis(trifluoro methanesulfonyl)imide (LiTf₂N, 99.95%) and bovine serum albumin (BSA, 98%) were purchased from Sigma-Aldrich and used as received. Azobisisobutyronitrile (AIBN, 98%, Tianjin Kaixin Chemical Company, China) was recrystallized from methanol before use and stored in the refrigerator. Carbon cloth (Toray TGP-H-060, Japan) was used for the substrate without any purification and pre-treatment. Nafion (Dupont D520, 5 wt % in ethanol) was purchased from Hesen Electrical Equipments Co., Ltd. (Shanghai, China). Platinum (20 wt% on carbon black, HiSPEC-3000) was brought from Alfa Aesar and used as received. All other reagents were commercially available and were used as received. Poly[1-cyanomethyl-3-vinylimidazolium bis(trifluoromethanesulfonyl)imide] (PIL-Tf₂N) was prepared according to a previous report.^[S1]

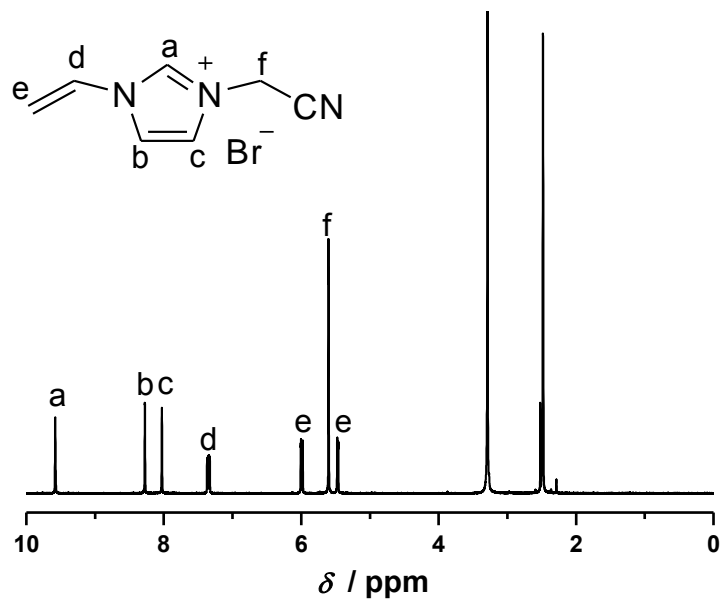


Figure S1 ^1H NMR spectrum (400 MHz) of 3-cyanomethyl-1-vinylimidazolium bromide (CMVIm-Br) in $\text{DMSO-}d^6$ at 25 °C.

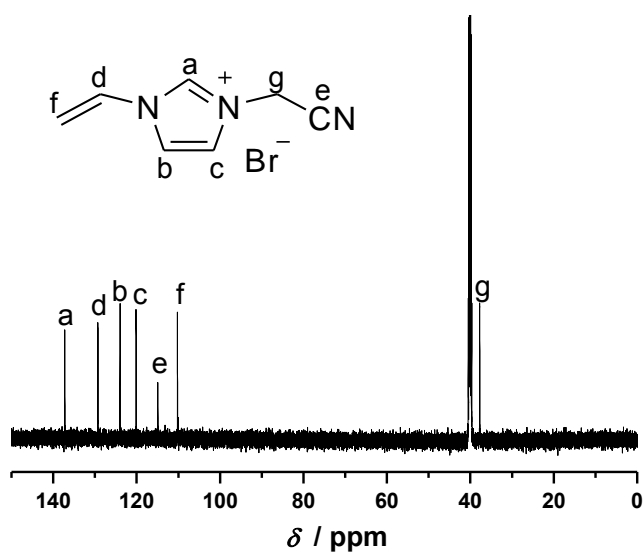


Figure S2 ^{13}C NMR spectrum (100 MHz) of 3-cyanomethyl-1-vinylimidazolium bromide (CMVIm-Br) in $\text{DMSO-}d^6$ at 25 °C.

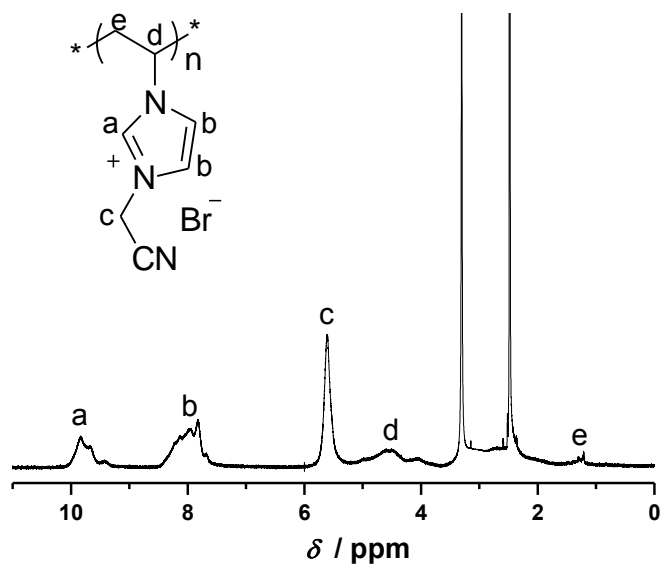


Figure S3 ^1H NMR spectrum (400 MHz) of poly(3-cyanomethyl-1-vinylimidazolium bromide) (PIL-Br) in DMSO- d_6 at 25 °C.

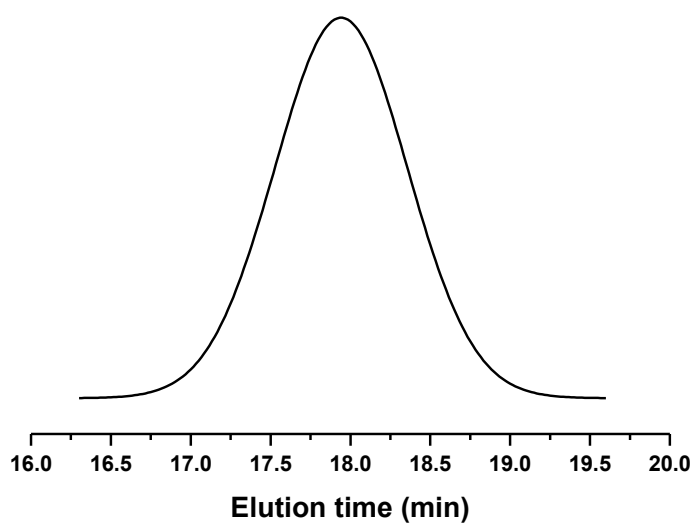


Figure S4 GPC trace of poly(3-cyanomethyl-1-vinylimidazolium bromide).

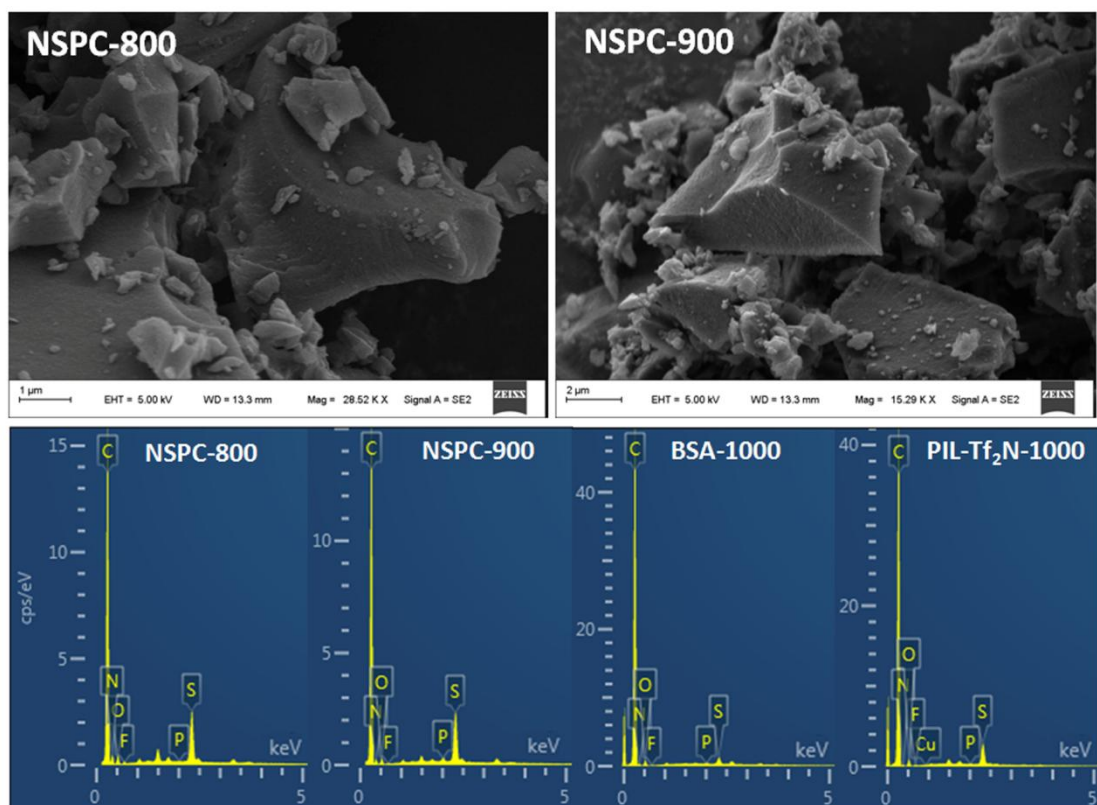


Figure S5 SEM images of different carbon materials (a NSPC-800, b NSPC-900) and energy dispersive X-ray (EDX) spectra of BSA-1000, PIL-Tf₂N-1000, NSPC-8000 and NSPC-900.



Figure S6. HRTEM image of NSPC-800. The white arrows point out the preferential orientation of the graphitic layers.

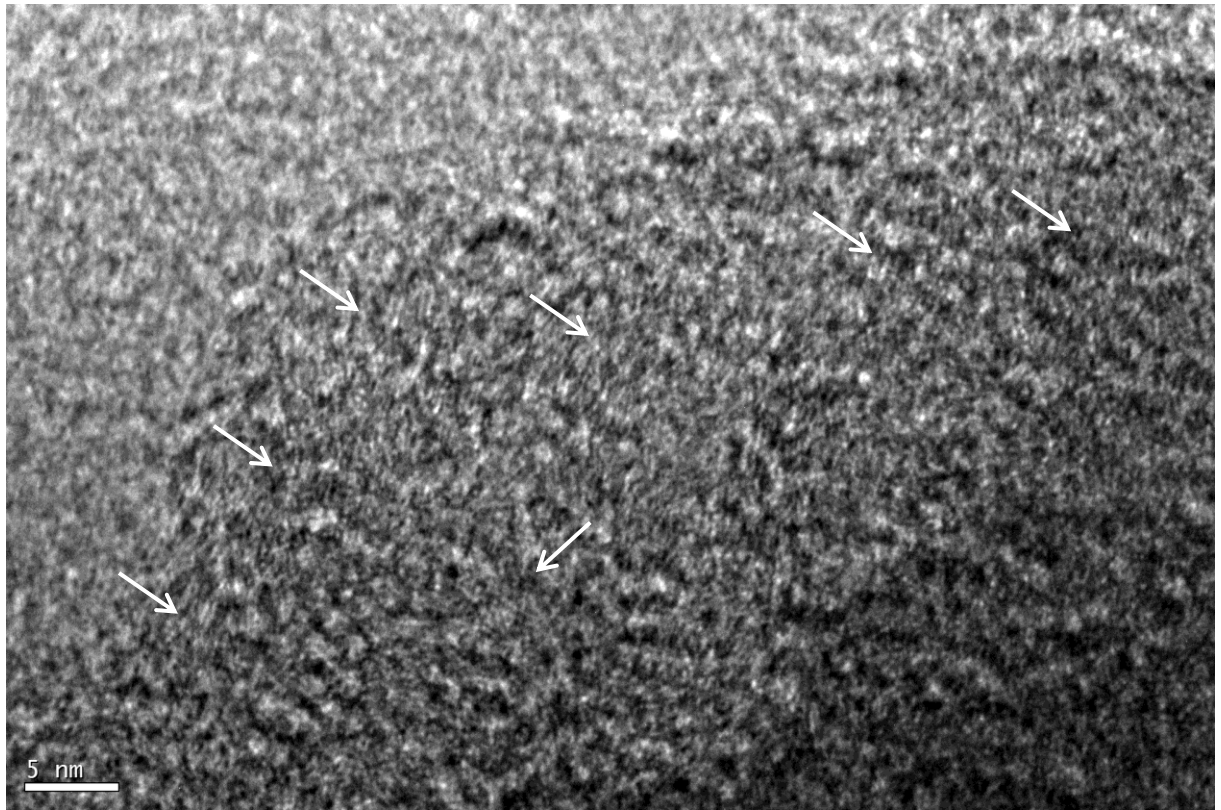


Figure S7. HRTEM image of NSPC-900. The white arrows point out the preferential orientation of the graphitic layers.

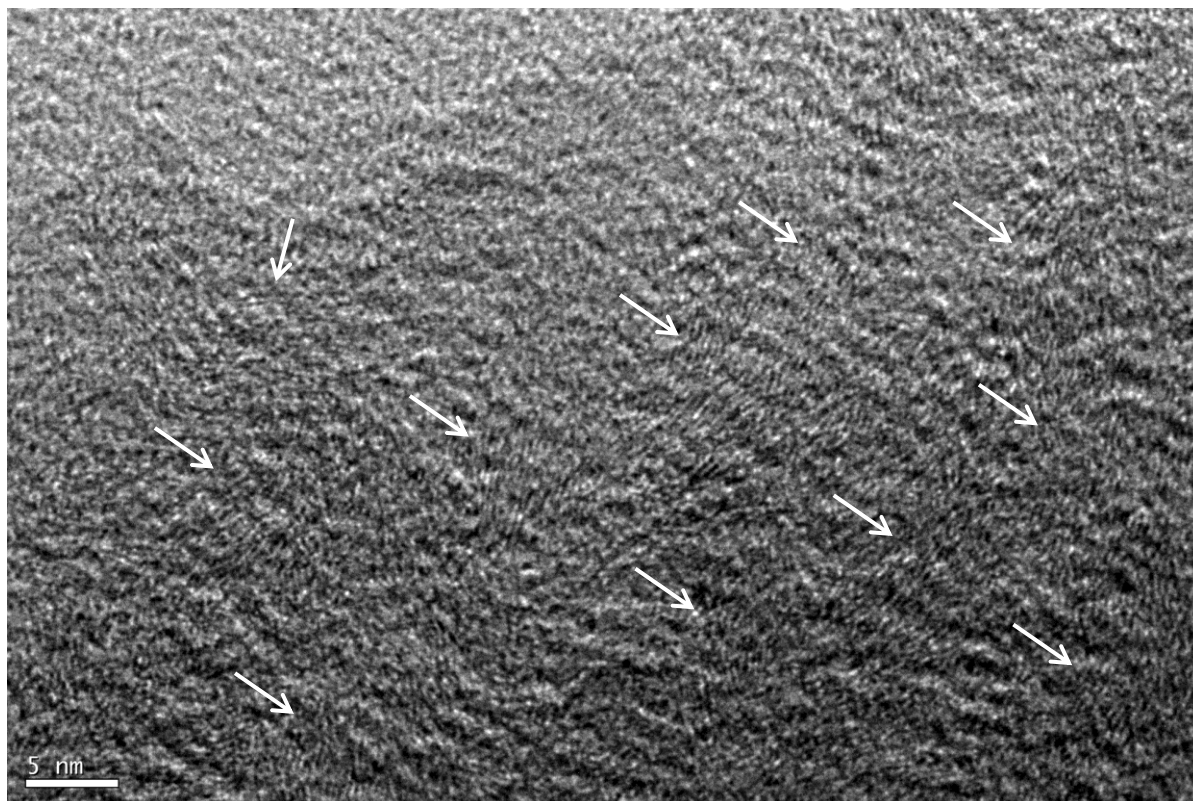


Figure S8. HRTEM image of NSPC-1000. The white arrows point out the preferential orientation of the graphitic layers.

Table S1 Element contain in different carbon materials determined by elemental analysis.

Sample	C	N	O	S
NSPC-800	60.81%	14.30%	2.102%	3.870%
NSPC-900	68.84%	9.11%	1.919%	3.318%
NSPC-1000	80.17%	3.58%	1.651%	2.009%
BSA-1000	81.97%	7.82%	0.792%	1.12%
PIL-Tf ₂ N-1000	80.27%	2.64%	1.592%	1.878%

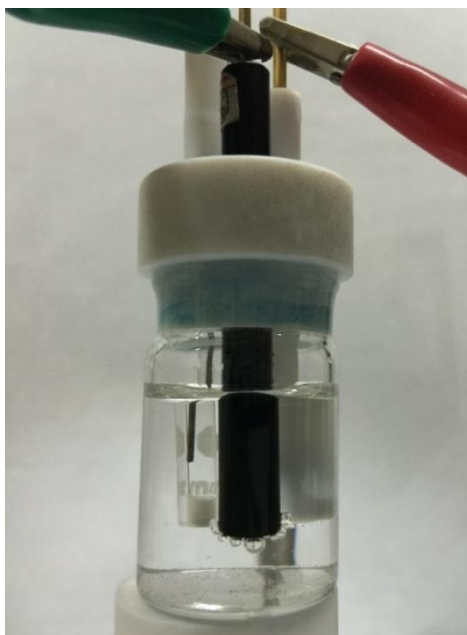


Figure S9 Photograph of the setup for HER test in 0.5 M H_2SO_4 showing the production of hydrogen bubbles on NSPC-1000-loaded glassy carbon electrode. The counter electrode and reference electrode are platinum wire electrode and saturated calomel electrode, respectively.

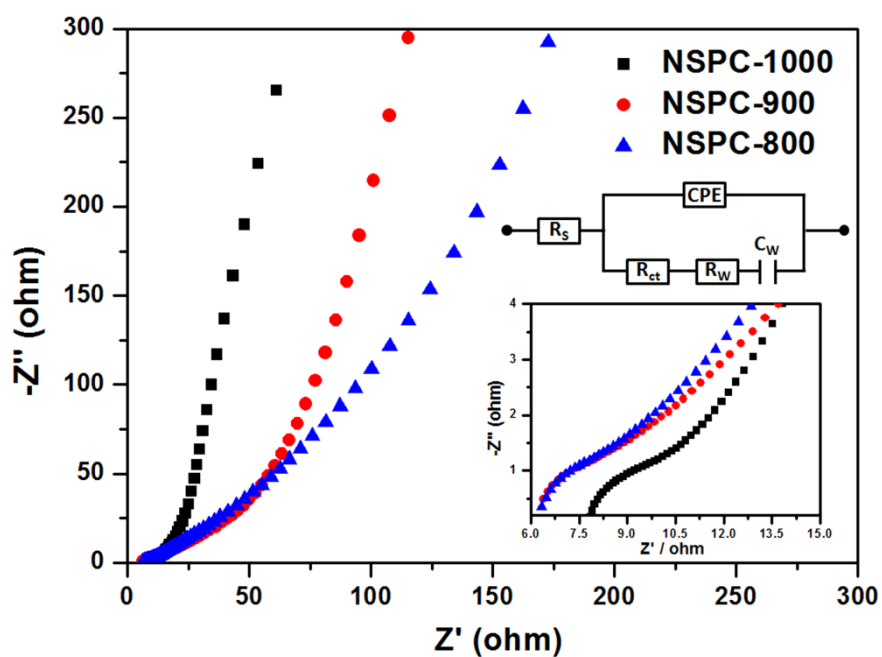


Figure S10 Electrochemical impedance spectroscopy (EIS) data for NSPC materials in H_2SO_4 (overpotential = 175 mV, 309 mV, 417 mV, corresponding to NSPC-1000, NSPC-900 and NSPC-800, respectively).

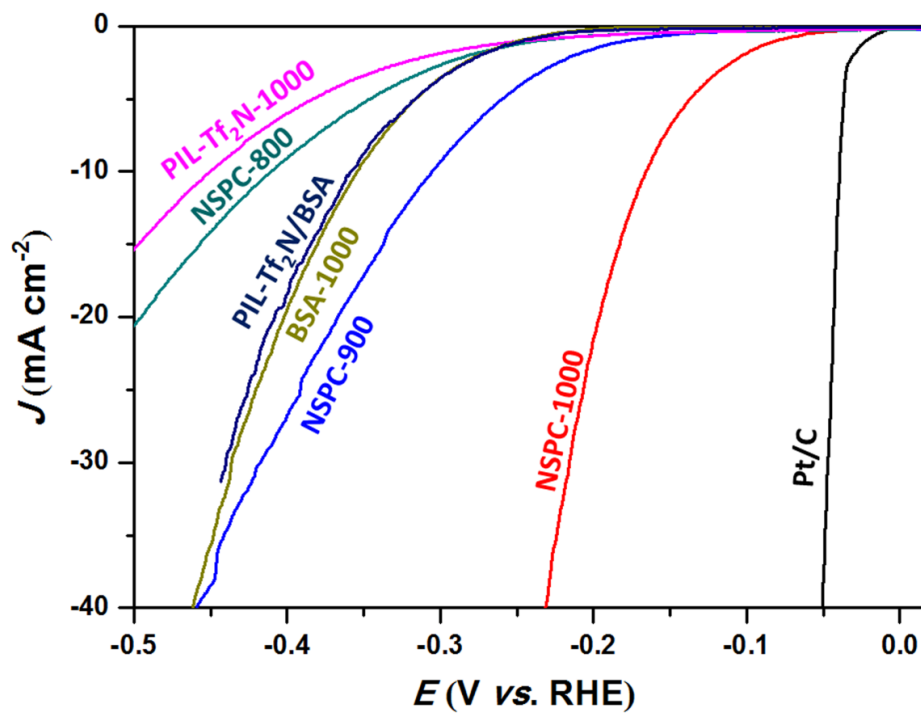


Figure S11 LSV curves of different carbon materials after iR correction of the data in Figure 4a (for HER test). In the iR-corrected data for HER, NSPC-1000 exhibits a current density of 10 mA cm^{-2} at the overpotential of 165 mV in 0.5 M H_2SO_4 solution.

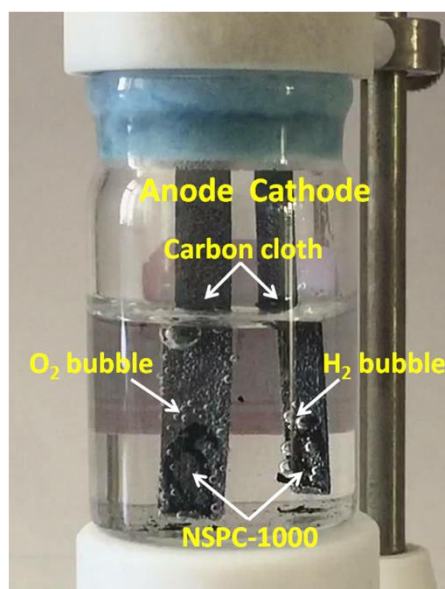


Figure S12 Photograph of the two-electrode setup showing the generation of hydrogen and oxygen bubbles on CC.

Table S2 HER performance of NSPC-1000 in this work, in comparison with the results of some representative carbon-based and non-noble electrocatalysts from recent publications.

Catalyst	Electrolyte	Overpotential at $j = 10 \text{ mA cm}^{-2}$ (mV)	Tafel slope (mV dec ⁻¹)	Ref.
C ₃ N ₄ /FTO	0.1 M PBS	250	/	S2
	0.1 M KOH	100		
C ₃ N ₄ @NG	0.5 M H ₂ SO ₄	240	51.5	S3
	0.1 M KOH	>600	/	
g-C ₃ N ₄ nanoribbon-G	0.5 M H ₂ SO ₄	207	54	S4
C ₃ N ₄	0.1 M PBS	600 (at $j = 0.8 \text{ mA cm}^{-2}$)	120	S5
	0.1 M KOH	300 (at $j = 0.8 \text{ mA cm}^{-2}$)		
MPSA/GO-1000	0.5 M H ₂ SO ₄	210 (at $j = 30 \text{ mA cm}^{-2}$)	/	S6
	0.1 M KOH	470	/	
N,P-graphene-1	0.5 M H ₂ SO ₄	420	/	S7
	0.1 M KOH	>600	/	
SNCTs	0.5 M H ₂ SO ₄	76 (at $j = 0.2 \text{ mA cm}^{-2}$)	126	S8
N,S codoped graphene 500C	0.5 M H ₂ SO ₄	276	81	S9
SHG	0.1 M KOH	310	112	S10
N-G	0.1 M KOH	510	157	S11
NiMoN _x /C	0.1 M HClO ₄	/	35.9	S12
Co-NRCNTs	0.5 M H ₂ SO ₄	260	69	S13
	0.1 M KOH	>400	/	
1T-MoS ₂ nanosheets	0.5 M H ₂ SO ₄	>200	41-46	S14

Exfoliated WS ₂ nanosheets	0.5 M H ₂ SO ₄	210 mV	60	S15
Exfoliated MoS ₂ nanosheets	0.5 M H ₂ SO ₄	195	54	S16
CoOx@CN	0.5 M H ₂ SO ₄	232	115	S17
Monolayer MoS ₂ supported by NPG	0.5 M H ₂ SO ₄	226	46	S18
NSPC-1000	0.5 M H ₂ SO ₄	172	44	<i>This</i>
	1.0 M KOH	234	59	<i>work</i>

Table S3. Comparison of the HER activity of NSPC-1000 in the present study and leading literature results.

Entry	Catalyst	Overpotential (mV)	Tafel slope (mV dec ⁻¹)	Electrolyte	Reference
1	SA900ZC (<i>S. aureus</i> cell)	200	58.4	0.5M H ₂ SO ₄	S19
2	HPC-900 (Human hair)	100	57.4	0.5M H ₂ SO ₄	S20
3	NPCSBF-1000 (Chinese steamed bread flour)	220	77	0.5M H ₂ SO ₄	S21
4	S/N-CLs (<i>Magnolia liliiflora</i> flowers)	90 (onset potential)	73	0.5 M H ₂ SO ₄	S22
5	CS-900 silk cocoon	317	173	0.5M H ₂ SO ₄	S23
6	MoS ₂ /SNCF Silk cocoon	102	60	0.5M H ₂ SO ₄	S24
7	MoP/CF sodium alginate	<200	56.4	0.5 M H ₂ SO ₄	S25
8	MoS ₂ /AC (Glucose)	80 (onset potential)	40	0.5 M H ₂ SO ₄	S26
9	NSPC-1000	172	44.3	0.5 M H ₂ SO ₄	This work
		234	58.9	1.0 M KOH	

Table S4 OER performance of NSPC-1000 in this work, in comparison with the results of some representative carbon-based electrocatalysts from recent publications.

Catalyst	Electrolyte	Overpotential at $j = 10 \text{ mA cm}^{-2}$ (V)	Tafel slope (mV dec ⁻¹)	Ref.
SHG	0.1 M KOH	1.60	71	S10
N-doping graphite	0.1 M KOH	1.61	/	S27
Oxidized carbon cloth	0.1 M KOH	1.72	82	S28
N, P-codoped graphene/ carbon nanosheets	0.1 M KOH	1.57	70	S29
N,O-codoped carbon hydrogen film	0.1 M KOH	1.63	141	S30
N, S-codoped G	0.1 M KOH	1.65	59	S31
N,O,P-tridoped porous carbon	1.0 M KOH	1.63	84	S32
N-doped G/CNTs hybrids	0.1 M KOH	1.63	83	S33
TCCN	0.1 M KOH	1.65	74.6	S34
MnxOy/NC, CoxOy/NC	0.1 M KOH	1.64–1.68	/	S35
N, O dual-doped carbon	0.1 M KOH	1.70	141	S36
Mn ₃ O ₄ /CoSe ₂	0.1 M KOH	1.68	49	S37
NiCo ₂ O ₄ -graphene	0.1 M KOH	1.69	156	S38
g-C ₃ N ₄ -graphene film	0.1 M KOH	1.65	128	S39
NSPC-1000	0.1 M KOH	1.69 (on GCE) 1.59 (on CC)	88 70	This work

Table S5. Comparison of capacitance performance of NSPC-1000 in the present study and leading literature results.

Entry	Material	Specific capacitance	Density of Current	Electrolyte	Reference
1	GA650	272 F/g	1 A/g	1 M H ₂ SO ₄	S40
2	HPC-650	312 F/g	1 A/g	1 M H ₂ SO ₄	S41
3	PHC-4	476 F cm ⁻³	1mV s ⁻¹	6 M KOH	S42
4	SSC	669 mF cm ⁻²	1 mA cm ⁻²	6 M KOH	S43
5	N-HC-800	275 F g ⁻¹	0.2 A/g	6 M KOH	R44
6	T-N-PC	411 F g ⁻¹	1 A/g	1 M Na ₂ SO ₄	S45
7	HCPC-800	217 F g ⁻¹	5 mV s ⁻¹	6 M KOH	S46
8	WB-PC-700	413 F g ⁻¹	1 A/g	6 M KOH	S47
9	NPCs	465 Fg ⁻¹	1 A/g	0.1 KOH	S48
10	NSPC-1000	495 Fg ⁻¹	0.1 A/g	1 M H ₂ SO ₄	This work

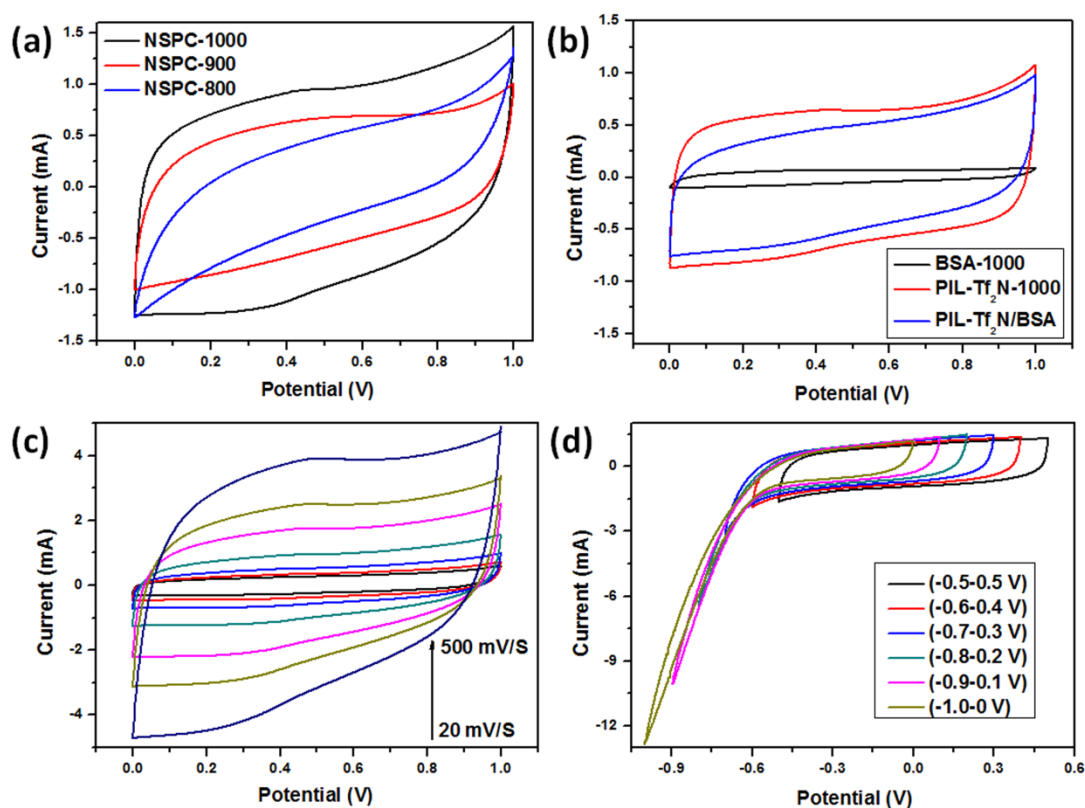


Figure S13 Electrochemical performances of carbon electrode materials. (a) Cyclic voltammetry (CV) profiles of NSPCs; (b) CV profiles of BSA-1000 and PIL-Tf₂N-1000 and PIL-Tf₂N/BSA (it was prepared by mixing PIL-Tf₂N-1000 and BSA-1000 (7:1, w/w)); (c) CV curves of NSPC-1000 at different scan rates; (d) CV curves of NSPC-1000 in different potential windows, scan rate 100 mV s⁻¹. All the measurements were conducted in 0.5 M H₂SO₄ electrolyte.

Supporting information, Video

Video S1: HER using NSPC-1000 loaded carbon cloth as both anode and cathode.

This movie shows the H₂ and O₂ evolution on NSPC-1000 loaded carbon cloth electrodes in the electrochemical cell at an applied potential from 0.1 to -0.7 V. (electrolyte: 0.5 M H₂SO₄; NSPC-1000 loading: 0.25 mg cm⁻²)

Reference

- [S1] J. Yuan, C. Giordano and M. Antonietti, *Chem. Mater.*, 2010, **22**, 5003.
- [S2] M. Shalom, S. Gimenez, F. Schipper, I. Herraiz-Cardona, J. Bisquert and M. Antonietti, *Angew. Chem. Int. Ed.*, 2014, **53**, 3654.
- [S3] Y. Zheng, Y. Jiao, Y. Zhu, L. H. Li, Y. Han, Y. Chen, A. Du, Mietek Jaroniec and Shi Zhang Qiao, *Nat. Commun.*, 2014, **5**, 3783.
- [S4] Y. Zhao, F. Zhao, X. Wang, C. Xu, Z. Zhang, G. Shi and L. Qu, *Angew. Chem. Int. Ed.*, 2014, **53**, 13934.
- [S5] M. Shalom, S. Gimenez, F. Schipper, I. Herraiz-Cardona, J. Bisquert and M. Antonietti, *Angew. Chem. Int. Ed.*, 2014, **126**, 3728.
- [S6] J. Zhang, L. Qu, G. Shi, J. Liu, J. Chen and L. Dai, *Angew. Chem. Int. Ed.*, 2016, **55**, 2230.
- [S7] Y. Zheng, Y. Jiao, L. H. Li, T. Xing, Y. Chen, M. Jaroniec and S. Z. Qiao, *ACS Nano.*, 2014, **8**, 5290.
- [S8] T. Sun, Q. Wu, Y. Jiang, Z. Zhang, L. Du, L. Yang, X. Wang and Z. Hu, *Chem. Eur. J.*, 2016, **22**, 10326.
- [S9] Y. Ito, W. Cong, T. Fujita, Z. Tang and M. Chen, *Angew. Chem. Int. Ed.*, 2015, **54**, 2131.
- [S10] C. Hu and L. Dai, *Adv. Mater.*, 2017, DOI: 10.1002/adma.201604942.
- [S11] J. M. Ge, B. Zhang, L. B. Lv, H. H. Wang, T. N. Ye, X. Wei, J. Su, K. X. Wang, X. H. Lin and J. S. Chen, *Nano Energy*, 2015, **15**, 567.
- [S12] W.F. Chen, K. Sasaki, C. Ma, A. I. Frenkel, N. Marinkovic, J. T. Muckerman, Y. Zhu and R. R. Adzic, *Angew. Chem. Int. Ed.*, 2012, **51**, 6131.
- [S13] X. Zou, X. Huang, A. Goswami, R. Silva, B. R. Sathe, E. Mikmekova and T. Asefa, *Angew. Chem. Int. Ed.*, 2014, **53**, 4372.
- [S14] D. Voiry, M. Salehi, R. Silva, T. Fujita, M. Chen, T. Asefa, V. B. Shenoy, Goki Eda and M. Chhowalla, *Nano Lett.*, 2013, **13**, 6222.
- [S15] D. Voiry, H. Yamaguchi, J. Li, R. Silva, D. C. B. Alves, Takeshi Fujita, M. Chen, T. Asefa, V. B. Shenoy, G. Eda and M. Chhowalla, *Nat. Mater.*, 2013, **12**, 850.
- [S16] M.A. Lukowski, A.S. Daniel, F. Meng, A. Forticaux, L. Li and S. Jin, *J. Am. Chem. Soc.*, 2013, **135**, 10274.
- [S17] H. Jin, J. Wang, D. Su, Z. Wei, Z. Pang and Y. Wang, *J. Am. Chem. Soc.*, 2015, **137**, 2688.

- [S18] Y. Tan, P. Liu, L. Chen, W. Cong, Y. Ito, J. Han, X. Guo, Z. Tang, T. Fujita, A. Hirata and M. W. Chen, *Adv. Mater.*, 2014, **26**, 8023.
- [S19] L. Wei, H. E. Karahan, K. Goh, W. Jiang, D. Yu, O. Birer, R. Jiang and Y. Chen, *J. Mater. Chem. A*, 2015, **3**, 7210.
- [S20] X. Liu, W. Zhou, L. Yang, L. Li, Z. Zhang, Y. Ke and S. Chen, *J. Mater. Chem. A*, 2015, **3**, 8840.
- [S21] A. Nsabimana, F. Wu, J. Lai, Z. Liu, R. Luque and G. Xu, *Electrochim. Acta*, 2018, **290**, 30.
- [S22] R. Atchudan, T. N. J. I. Edison, S. Perumal, A. S. Parveen and Y. R. Lee, *J. Electroanal. Chem.*, 2019, **833**, 357.
- [S23] X. Liu, M. Zhang, D. Yu, T. Li, M. Wan, H. Zhu, M. Du and J. Yao, *Electrochim. Acta*, 2016, **215**, 223.
- [S24] Q. F. Wang, R. P. Yanzhang, X. N. Ren, H. Zhu, M. Zhang and M. L. Du, *Int. J. Hydrogen Energy*, 2016, **41**, 21870.
- [S25] W. Cui, Q. Liu, Z. Xing, A. M. Asiri, K. A. Alamry and X. Sun, *Appl. Catal. B Environ.*, 2015, **164**, 144.
- [S26] X. Zhao, H. Zhu and X. Yang, *Nanoscale*, 2014, **6**, 10680.
- [S27] Y. Zhao, R. H. Nakamura, K. Kamiya, S. J. Nakanishi and K. Hashimoto, *Nat. Comm.*, 2013, **4**, 2390.
- [S28] N. Y. Cheng, Q. Liu, J. Q. Tian, Y. R. Xue, A. M. Asiri, H. F. Jiang, Y. Q. Hee and X. P. Sun, *Chem. Comm.*, 2015, **51**, 1616.
- [S29] R. Li, Z. D. Wei and X. L. Gou, *ACS Catal.*, 2015, **5**, 4133.
- [S30] S. Chen, J. J. Duan, M. Jaroniec and S. Z. Qiao, *Adv. Mater.*, 2014, **26**, 2925.
- [S31] K. G. Qu, Y. Zheng, S. Dai and S. Z. Qiao, *Nano Energy*, 2016, **19**, 373.
- [S32] J. P. Lai, S. P. Li, F. X. Wu, M. Saqib, R. Luque and G. B. Xu, *Energy Environ. Sci.*, 2016, **9**, 1210.
- [S33] G. L. Tian, M. Q. Zhao, D. S. Yu, X. Y. Kong, J. Q. Huang, Q. Zhang and F. Wei, *Small*, 2014, **10**, 2251.
- [S34] T. Y. Ma, J. L. Cao, M. Jaroniec and S. Z. Qiao, *Angew. Chem. Int. Ed.*, 2016, **55**, 1138.
- [S35] J. Masa, W. Xia, I. Sinev, A. Zhao, Z. Sun, S. Gruzke, P. Weide, M. Muhler and W. Schuhmann, *Angew. Chem. Int. Ed.*, 2014, **53**, 8508.
- [S36] S. Chen, J. J. Duan, M. Jaroniec and S. Z. Qiao, *Adv. Mater.*, 2014, **26**, 2925.

- [S37] M. R. Gao, Y. F. Xu, J. Jiang, Y. R. Zheng and S. H. Yu, *J. Am. Chem. Soc.*, 2012, **134**, 2930.
- [S38] S. Chen and S. Z. Qiao, *ACS Nano*, 2013, **7**, 10190.
- [S39] S. Chen, J. J. Duan, J. Ran and S. Z. Qiao, *Adv. Sci.*, 2015, **2**, 1400015.
- [S40] L. L. Zhang, H. H. Li, Y. H. Shi, C. Y. Fan, X. L. Wu, H. F. Wang, H. Z. Sun and J. P. Zhang, *ACS Appl. Mater. Interfaces*, 2016, **8**, 4233.
- [S41] Y. Shi, L. Zhang, T. B. Schon, H. Li, C. Fan, X. Li, H. Wang, X. Wu, H. Xie, H. Sun, D. S. Seferos and J. Zhang, *ACS Appl. Mater. Interfaces*, 2017, **9**, 42699.
- [S42] X. Liu, C. Ma, J. Li, B. Zielinska, R. J. Kalenczuk, X. Chen, P. K. Chu, T. Tang, E. Mijowska, *J. Power Sources*, 2019, **412**, 1.
- [S43] Y. Zhang, H. Jiang, Q. Wang, J. Zheng, C. Meng, *Applied Surface Science*, 2018, **447**, 876.
- [S44] Wei Liu, Jie Mei, Guolong Liu, Qian Kou, Tingfeng Yi, and Saijun Xiao, *ACS Sustainable Chem. Eng.*, 2018, **6**, 11595.
- [S45] Y. Ding, L. Mo, C. Gao, X. Liu, T. Yu, W. Chen, S. Chen, Z. Li and L. Hu, *ACS Sustainable Chem. Eng.*, 2018, **6**, 9822.
- [S46] L. Peng, Y. Cai, Y. Luo, G. Yuan, J. Huang, C. Hu, H. Dong, Y. Xiao, Y. Liang, Y. Liu and M. Zheng, *ACS Sustainable Chem. Eng.*, 2018, **6**, 12716.
- [S47] P. Yu, Y. Liang, H. Dong, H. Hu, S. Liu, L. Peng, M. Zheng, Y. Xiao, and Y. Liu, *ACS Sustainable Chem. Eng.*, 2018, **6**, 15325.
- [S48] G. Ren, Y. Li, Q. Chen, Y. Qian, J. Zheng, Y. Zhu and C. Teng, *ACS Sustainable Chem. Eng.*, 2018, **6**, 16032.