Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Heterogeneous Co-CN nanofibers with controlled active terminal N sites for hydrogen evolution reaction

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1. Experimental

1.1. Reagents and chemicals

Polyacrylonitrile (PAN, Mw = 150,000) was purchased from Sigma-Aldrich Co. Ltd. Cobalt (II) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$) and N, N-dimethylformamide (DMF) were purchased from Shantou Xilong Chemical Industry Incorporated Co., Ltd. The commercial Pt/C catalyst (with 20 wt% Pt on carbon black) was purchased from Alfa Aesar. All the reagents have reached the degree of analytical reagent. Ultrapure water (Millipore Milli-Q grade) with a resistivity of 18.2 MΩ was used in all the experiments.

1.2. Materials characterization

The morphology and microstructure of the catalysts were characterized by scanning electron microscopy (SEM, Hitachi S-4800), transmission electron microscopy (TEM, FEI Tecnai G20) and high-resolution transmission electron microscopy (HRTEM, FEI Tecnai F20) operated at 200 kV. Powder X-ray diffraction (XRD) patterns were collected on a Rigaku D/max 2500 diffract meter with Cu K radiation (λ=1.54056 Å). The Co contents of Co-CN nanofibers were determined by ICP-MS (PerkinElmer NexION 300X), and the C and N contents were analyzed by CHN elemental analysis (Vario MACRO). The X-ray photoelectron spectroscopy (XPS) were performed by an ESCALAB 250 Xi XPS system of Thermo Scientific, where the analysis chamber was 1.5×10^{-9} mbar and the X-ray spot was 500 nm.

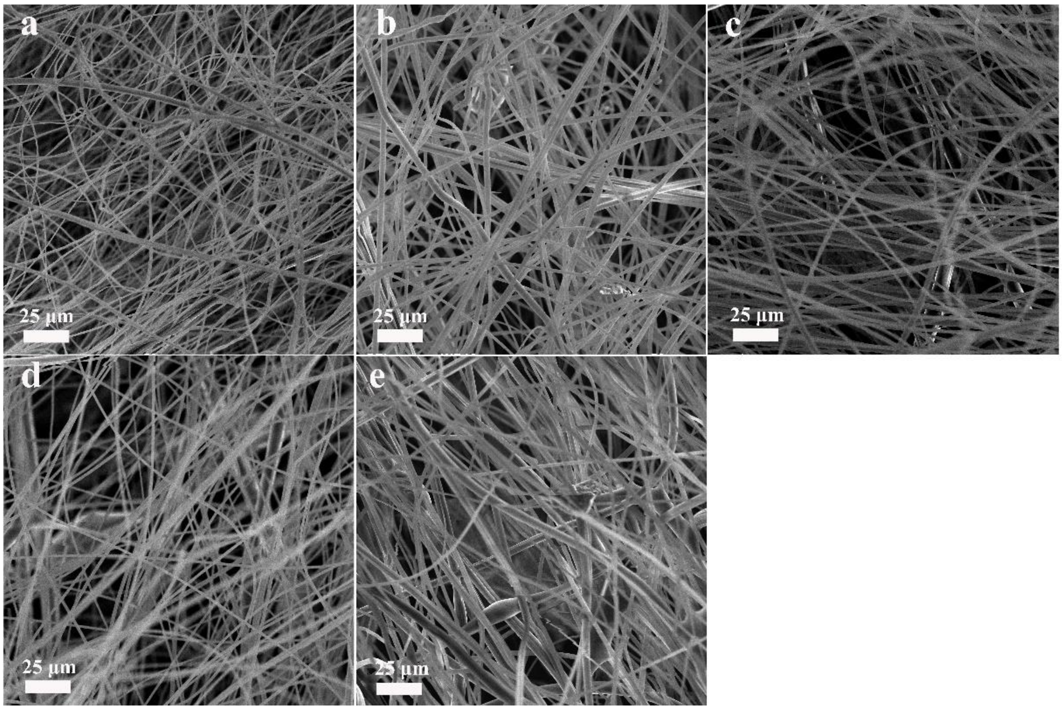

Fig. S1 SEM images of the (a) Co0-PAN, (b) Co2-PAN, (c) Co5-PAN, (d) Co10-PAN and (e) Co20-PAN fibers.

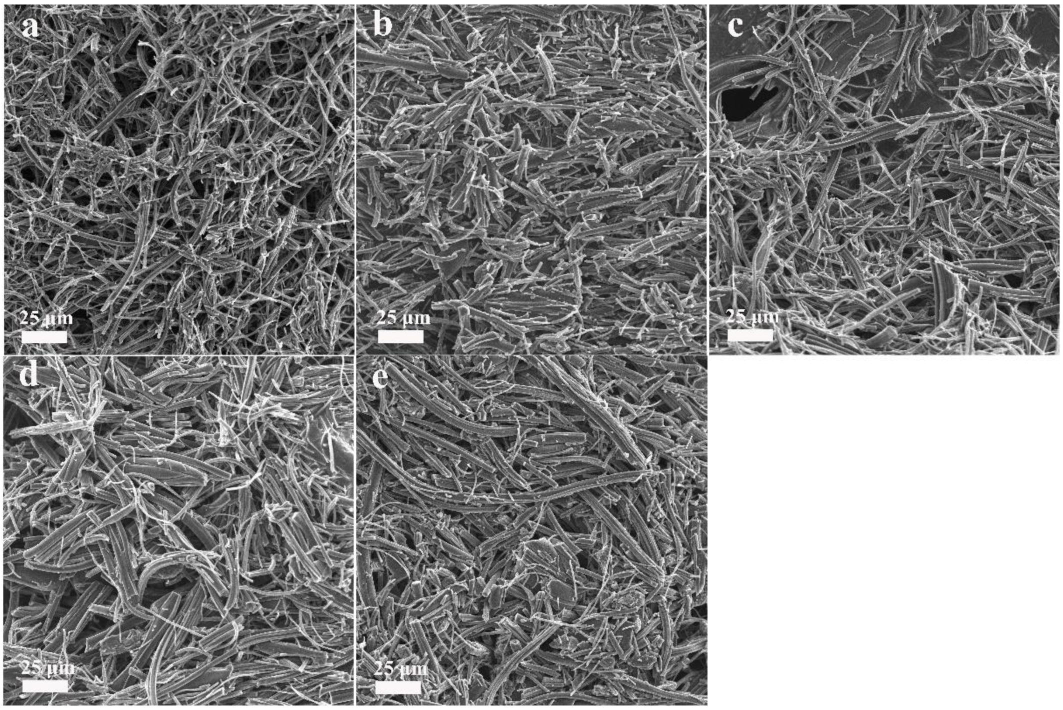

Fig. S2 SEM images of the (a) Co0-CN, (b) Co2-CN, (c) Co5-CN, (d) Co10-CN and (e) Co20-CN nanofibers.

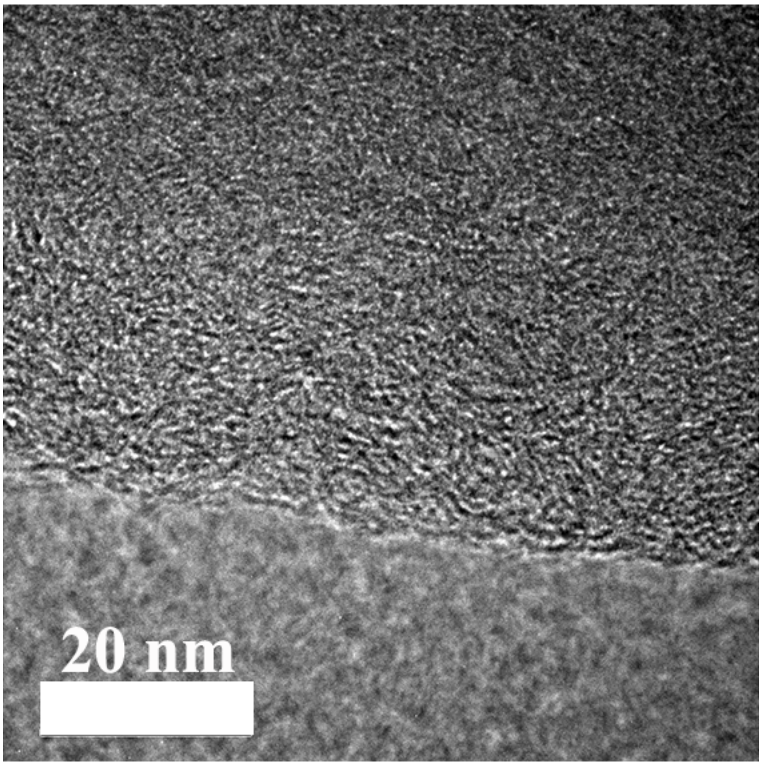

Fig. S3 HRTEM image of Co0-CN nanofiber.

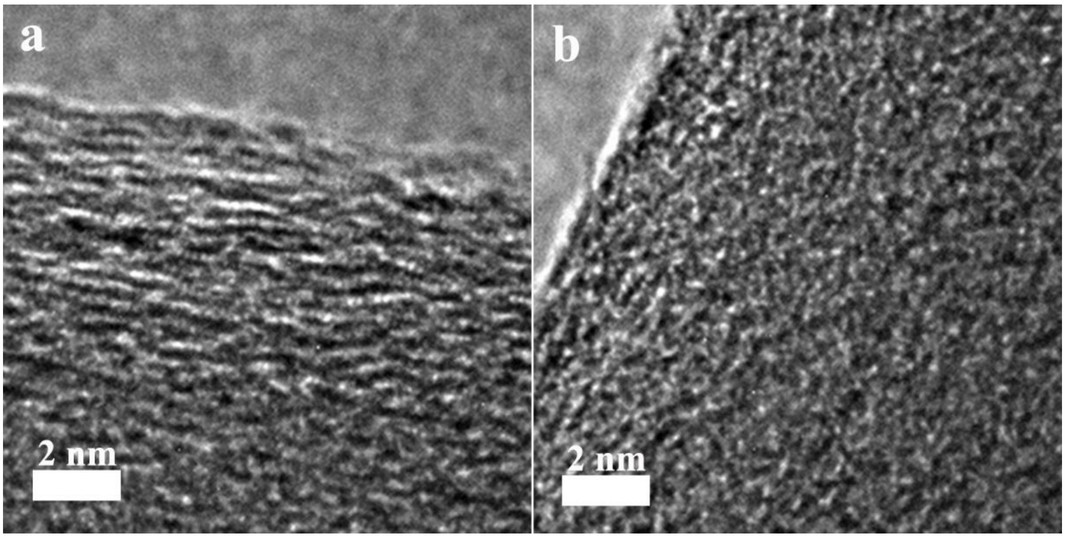

Fig. S4 The comparison on HRTEM images of the (a) Co0-CN and (b) Co2-CN nanofibers.

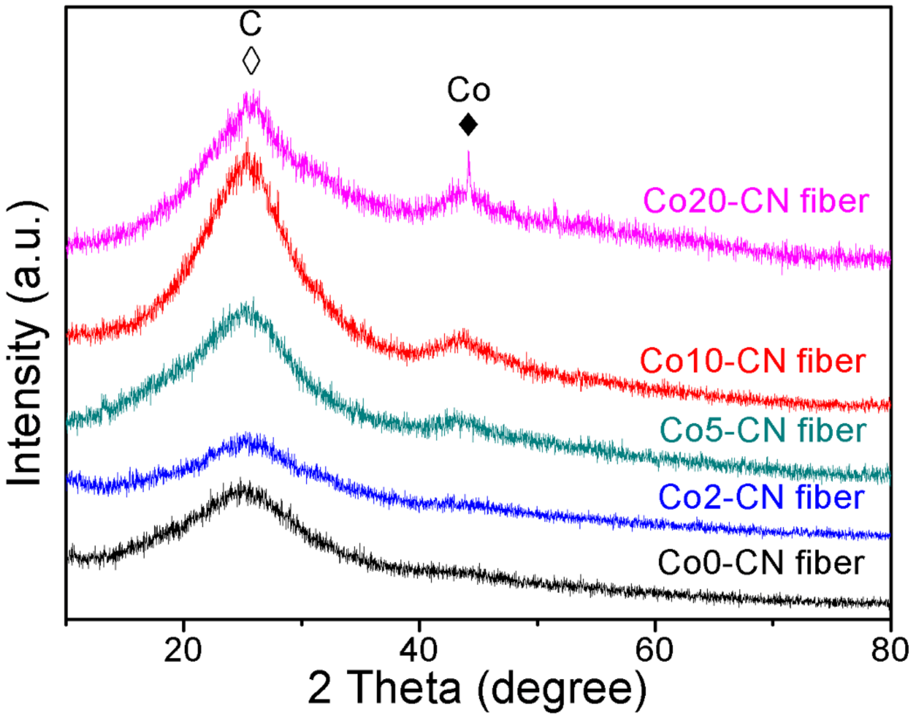

Fig. S5 XRD patterns of the Co0-CN, Co2-CN, Co5-CN, Co10-CN and Co20-CN nanofibers.

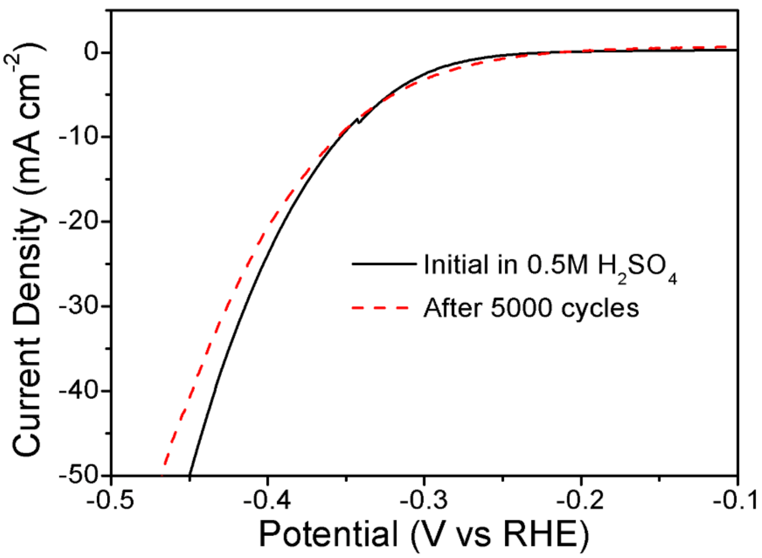

Fig. S6 Polarization curves recorded in 0.5 M H_2SO_4 at 10 mV s^{-1} for Co10-CN nanofiber before and after 5000 cycles from 0.5 to -0.5 V vs RHE at 100 mV s^{-1} under acid condition.

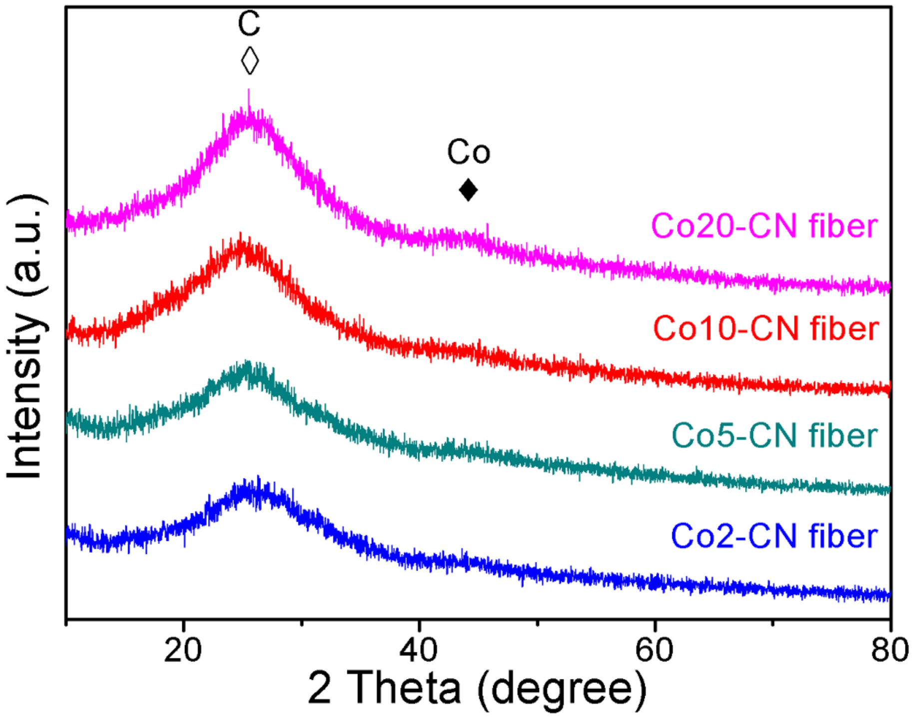

Fig. S7 XRD patterns of the Co2-CN, Co5-CN, Co10-CN and Co20-CN nanofibers after acid etching.

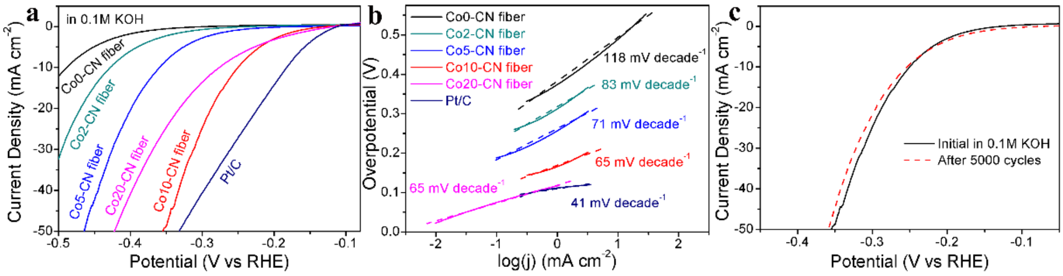

Fig. S8 Electrochemical characterizations for HER activity in 0.1 M KOH. (a) Polarization curves obtained at 10 mV s^{-1} for Co0-CN, Co2-CN, Co5-CN, Co10-CN, Co20-CN nanofibers and Pt/C catalyst; (b) Tafel plots of the corresponding samples; (c) Polarization curves recorded at 10 mV s^{-1} for Co10-CN nanofiber before and after 5000 cycles from 0.5 to -0.5 V vs RHE at 100 mV s^{-1} under basic condition.

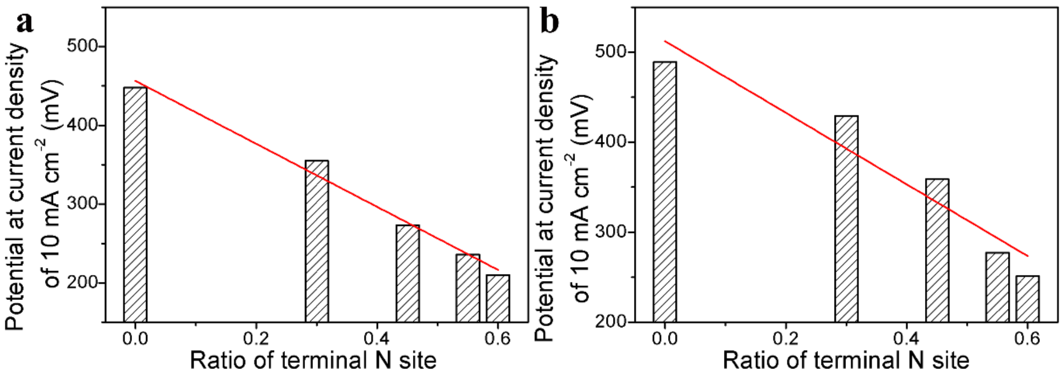

Fig. S9 The structure-activity relationship between ratio of terminal N site and potential at current density of 10 mA cm^{-2} in the Co0-CN, Co2-CN, Co5-CN, Co20-CN and Co10-CN nanofibers under (a) acidic and (b) alkaline conditions.

Table S1. The characteristic data of the Co-CN nanofibers

Samples	Element content (%)			Overpotential to deliver 10 mA cm^{-2} (mV)		Impedance[c] (Ω)
	Co[a]	C[b]	N[b]	H_2SO_4	KOH	
Co0-CN fiber	0	40.25	9.52	448	489	21.3
Co2-CN fiber	1.86	39.51	10.04	355	429	18.9
Co5-CN fiber	5.02	37.62	9.79	273	359	18.8
Co10-CN fiber	9.64	35.83	9.84	210	251	18.5
Co20-CN fiber	18.75	30.39	9.61	236	277	18.4

a Co loading amount in different samples is determined by the mass of Co element with ICP-MS analysis.

b C and N content were measured by the X-ray photoelectron spectroscopy and CHN element analysis.

c The impedance was obtained via the fitting data using the ZView software.

Table S2. Results of XPS data of N element in the Co-CN nanofibers

Samples	Species peak are[a]			Ratio of terminal N
	terminal N [a]	Co-N_x	graphitic N	
Co0-CN fiber	0	0	6352.4	0
Co2-CN fiber	1459.6	2409.5	922.0	0.3
Co5-CN fiber	1935.1	1678.8	723.3	0.45
Co20-CN fiber	3846.9	709.3	2424.3	0.55
Co10-CN fiber	3242.1	733.4	1452.9	0.6

a Peak area was calculated under the assumption that three N species occupy identical areas and have identical atomic sensitivity factors

Table S3. Comparison of HER performance of Co10-CN nanofiber with those reported Co-based and N-based electrocatalysts in acid electrolytes

Catalysts	η_{10} (mV)	Electrolytes	References
Co10-CN nanofiber	210	0.5 M H_2SO_4	**This work**
Co@NG	147	0.5 M H_2SO_4	S1
Co@NCNTs	260	0.5 M H_2SO_4	S2
Co-CN-600	181	0.5 M H_2SO_4	S3
NCN-1000-5	150	0.5 M H_2SO_4	S4
NDC-900	280	1.0 M H_2SO_4	S5
NC	140	0.5 M H_2SO_4	S6
C_3N_4-CNT-CF	240	0.5 M H_2SO_4	S7
ONPPGC/OCC	380	0.5 M H_2SO_4	S8

Table S4. Comparison of HER performance of Co10-CN nanofiber with those reported Co-based and N-based electrocatalysts in alkaline electrolytes

Catalysts	η_{10} (mV)	Electrolytes	References
Co10-CN nanofiber	251	0.1 M KOH	**This work**
Co-N/GF-900	165	1.0 M KOH	S9
$(Co\text{-}NMC)_1/NC$	220	0.1 M KOH	S10
Co@NG	220	1.0 M KOH	S11
Co-NG	273	1.0 M KOH	S1
Co-NRCNTs	370	1.0 M KOH	S2
CoO_x@CN	232	1.0 M KOH	S12
Co@N-C	210	1.0 M KOH	S13

Supplementary References

[1] H. Fei, J. Dong, M.J. Arellano-Jiménez, G. Ye, N.D. Kim, E.L. Samuel, Z. Peng, Z. Zhu, F. Qin, J. Bao, Atomic cobalt on nitrogen-doped graphene for hydrogen generation, ***Nat. Commun.***, 2015, 6, 8668.

[2] X. Zou, X. Huang, A. Goswami, R. Silva, B. R. Sathe, E. Mikmekova, T. Asefa, Cobalt-Embedded Nitrogen-Rich Carbon Nanotubes Efficiently Catalyze Hydrogen Evolution Reaction at All pH Values, ***Angew. Chem. Int. Ed.***, 2014, 53, 4372-4376.

[3] J. Chen, H. Zhou, Y. Huang, H. Yu, F. Huang, F. Zheng, S. Li, A 3D Co-CN framework as a high performance electrocatalyst for the hydrogen evolution reaction, ***RSC Adv.***,2016, 6, 42014-42018.

[4] H. Jiang, J. Gu, X. Zheng, M. Liu, X. Qiu, L. Wang, W. Li, Z. Chen, X. Ji, J. Li, Defect-rich and ultrathin N doped carbon nanosheets as advanced trifunctional metal-free electrocatalysts for the ORR, OER and HER, ***Energy Environ. Sci.***, 2019, 12, 322-333.

[5] D. K. Singh, R. N. Jenjeti, S. Sampath, M. Eswaramoorthy, Two in one: N-doped tubular carbon nanostructure as an efficient metal-free dual electrocatalyst for hydrogen evolution and oxygen reduction reactions, ***J. Mater. Chem. A.***, 2017, 5, 6025-6031.

[6] X. Liu, M. Zhang, D. Yu, T. Li, M. Wan, H. Zhu, Functional materials from nature: honeycomb-like carbon nanosheets derived from silk cocoon as excellent electrocatalysts for hydrogen evolution reaction, ***Electrochim. Acta***, 2016, 215, 223-230.

[7] Z. Peng, S. Yang, D. Jia, P. Da, P. He, A. M. Al-Enizi, Homologous metal-free electrocatalysts grown on three-dimensional carbon networks for overall water splitting in acidic and alkaline media, ***J. Mater. Chem. A.***, 2016, 4, 12878-12883.

[8] J. Lai, S. Li, F. Wu, M. Saqib, R. Luque, G. Xu. Unprecedented metal-free 3D porous carbonaceous electrodes for full water splitting, ***Energy Environ. Sci.***, 2016, 9, 1210-1214.

[9] Y. Tong, X. Yu, H. Wang, B. Yao, C. Li, G. Shi, Trace Level Co-N Doped Graphite Foams as High-Performance Self-Standing Electrocatalytic Electrodes for Hydrogen and Oxygen Evolution, ***ACS Catal.***, 2018, 8, 4637-4644.

[10] B. Bayatsarmadi, Y. Zheng, Y. Tang, M. Jaroniec, S.-Z. Qiao, Significant Enhancement of Water Splitting Activity of N-Carbon Electrocatalyst by Trace Level Co Doping, ***Small***, 2016, 12, 3703-3711.

[11] M. Zeng, Y. Liu, F. Zhao, K. Nie, N. Han, X. Wang, W. Huang, X. Song, J. Zhong, Y. Li, Metallic Cobalt Nanoparticles Encapsulated in Nitrogen-Enriched Graphene Shells: Its Bifunctional Electrocatalysis and Application in Zinc-Air Batteries, ***Adv. Funct. Mater.***, 2016, 26, 4397-4404.
[12] H. Jin, J. Wang, D. Su, Z. Wei, Z. Pang, Y. Wang, In Situ Cobalt-Cobalt Oxide/N-Doped Carbon Hybrids as Superior Bifunctional Electrocatalysts for Hydrogen and Oxygen Evolution, ***J. Am. Chem. Soc.***, 2015, 137, 2688-2694.
[13] J. Wang, D. F. Gao, G. X. Wang, S. Miao, H. H. Wu, J. Y. Li, X. H. Bao, Cobalt Nanoparticles Encapsulated in Nitrogen-Doped Carbon as a Bifunctional Catalyst for Water Electrolysis, ***J. Mater. Chem. A***, 2014, 2, 20067-20074.