Supporting Information

Optimized Synthesis of Nitrogen and Phosphorus Dual-Doped Coal-Based Carbon Fiber Supported Pd Catalyst with Enhanced Activities for Formic Acid Electrooxidation

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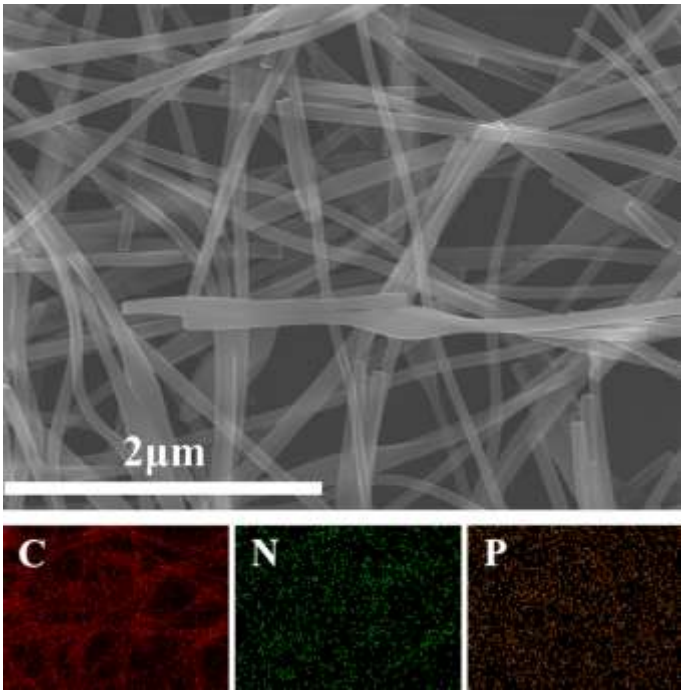

Figure S1. Elemental mapping of C, N and P in the NP-Coal-CFs(DCD/TPP)

Table S1. Surface parameters of the coal-based CFs

Sample ID	S_{BET}[a] ($m^2\ g^{-1}$)	V_{total}[b] ($cm^2\ g^{-1}$)	V_{meso}[c] ($cm^2\ g^{-1}$)	V_{micro}[d] ($cm^2\ g^{-1}$)	D_{ap}[e] (nm)
Coal-CFs	431.67	0.208	0.055	0.167	1.92
N-Coal-CFs(DCD)	474.32	0.220	0.053	0.182	1.85
P-Coal-CFs(TPP)	367.91	0.197	0.075	0.142	2.14
NP-Coal-CFs(DCD/TPP)	503.54	0.230	0.050	0.194	1.83

[a] S_{BET}: specific surface area calculated by the BET method.

[b] V_{total}: total pore volume at P/P_0=0.99.

[c] V_{meso}: volume of mesopore (1.9-51.2 nm) calculated using the BJH method.

[d] V_{micro}: volume of micropore calculated by the H-K (Original) method.

[e] Dap: average pore size.

Table S2. Physical characteristic of catalysts

Catalysts	Pd (111) at 2θ (◦)	d (111) (Å)	Lattice parameter (Å)	Crystallite size (nm)	Particle size by TEM (nm)
Pd/Coal-CFs	40.262	2.2381	3.8765	10.8	12.2
Pd/N-Coal-CFs(DCD)	40.327	2.2346	3.8705	4.5	7.6
Pd/P-Coal-CFs(TPP)	40.298	2.2362	3.8731	4.2	7.2
Pd/NP-Coal-CFs(DCD/TPP)	40.345	2.2337	3.8330	3.8	5.3

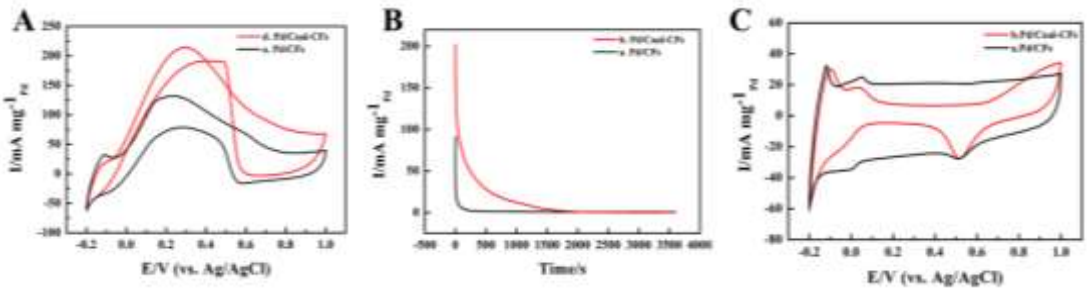

Figure S2. Electrochemical analysis data of (A) CV curves; (B) Amperometric i-t curves; (C) CV in 0.5 mol L^{-1} H_2SO_4 solution. (a) Pd/CFs; (b) Pd/Coal-CFs

Table S3. Comparison of electrochemical catalytic analysis

Sample	Pd wt %	ECSA (m^2/g)	Current density (mA mg^{-1} $_{Pd}$)
Pd/CFs	18.76 %	16.23	130.56
Pd/Coal-CFs	19.79%	30.40	214.30

Pure PAN fibers were prepared by electrospinning, and used it as support to prepare Pd/CFs catalyst, and its electrochemical performance was tested. The results are shown in the Figure S2 and Table S3. Obviously, the electrochemical performance of Pd/Coal-CFs catalyst after coal addition is enhanced. The increase in performance after the addition of coal may be due to the specific surface area, defect and disorder can be increased by adding coal in a suitable proportion.[1,2]

Table S4. Elemental contents of raw coal and acid treated coal

Sample	C wt%	O wt%	N wt%	S wt%
raw coal (EDS)	84.37	15.55	−	0.08
raw coal (industrial analysis)	81.24	9.29	−	0.26
acid treated coal (EDS)	55.34	44.05	−	0.61
Coal-CF	84.30	10.67	5.03	−

The EDS test of raw coal and acid-treated coal as shown in Table S4 has been carried out, and also compared with the industrial analysis value of raw coal. In raw coal and acid treated coal, only the elements of C, O and S were detected, and no other elements were detected. The content of oxygen and sulfur in acid treated coal increased after acidizing treatment because H_2SO_4 and HNO_3 added a number of sulfur and oxygen functional groups to the raw coal, making the acid treated coal soluble in *N*,*N*-dimethylformamide solvents.[1] As a comparison, Coal-CFs carbonized at 800 ℃ was also tested by EDS shown in Table S4. The elements of C, O and N were detected and no S elements was detected in Coal-CFs, which may be due to the fact that the content of S in acid treated coal used for spinning is only 0.61%, and volatilized in the form of gas in the process of 800 ℃ carbonization. This may be one of the reasons for specific surface area, defect and disorder of Coal-CF can be increased.

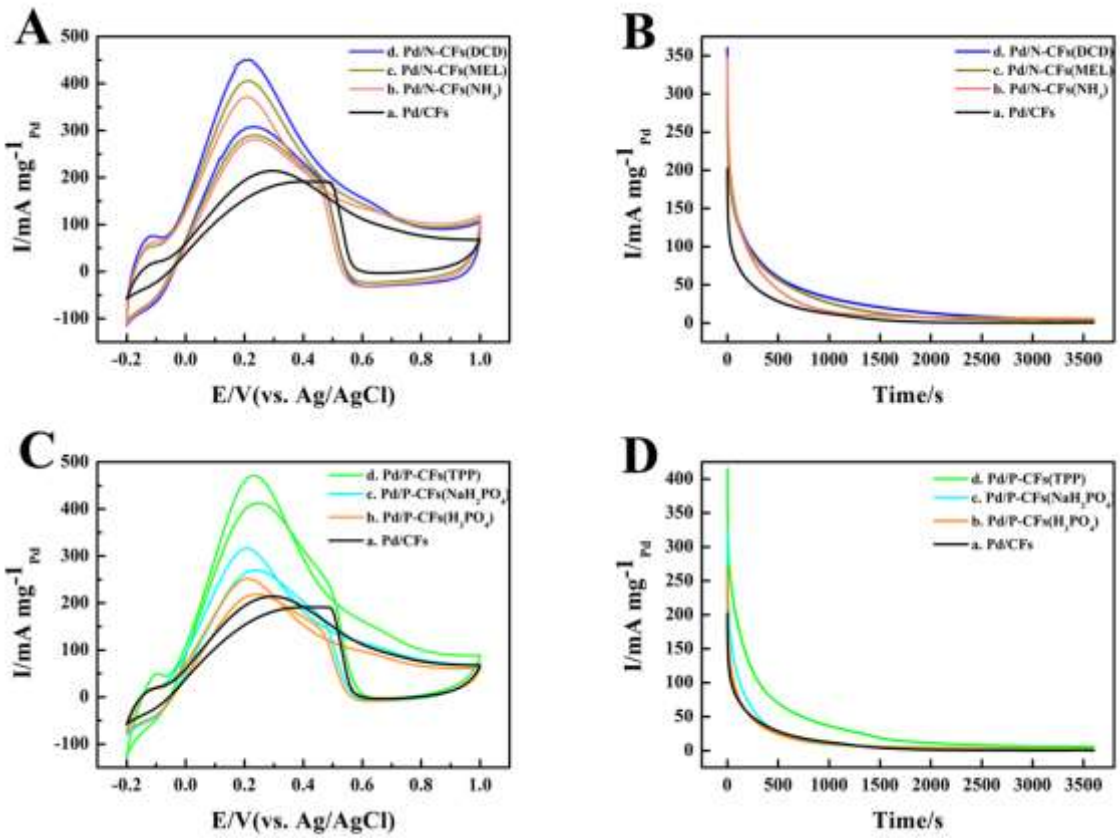

Figure S3. (A) CV curves and corresponding (B) Amperometric i-t curves of (a) Pd/Coal-CFs; (b) Pd/N-Coal-CFs(NH_3); (c) Pd/N-Coal-CFs(MEL); (d) Pd/N-Coal-CFs(DCD). (C) CV curves and corresponding (D) Amperometric i-t curves of (a) Pd/Coal-CFs; (b) Pd/P-Coal-CFs(H_3PO_4); (c) Pd/P-Coal-CFs(NaH_2PO_4); (d) Pd/P-Coal-CFs(TPP). In 0.5 mol L^{-1} H_2SO_4 and 0.5 mol L^{-1} HCOOH solution

Figure S3A describes the formic acid oxidition cyclic voltammograms (CV) of Pd/Coal-CFs, Pd/N-Coal-CFs(NH_3) Pd/N-Coal-CFs(MEL) and Pd/N-Coal-CFs(DCD) catalysts, the corresponding amperometric i-t curves with constant potential of 0.15 V is shown in Figure S3B. The mass specific activity of Pd/Coal-CFs, Pd/N-Coal-CFs(NH_3) Pd/N-Coal-CFs(MEL) and Pd/N-Coal-CFs(DCD) catalysts is 214.3, 370.6, 405.5 and 450.0 mA mg^{-1} $_{Pd}$, respectively. For comparison, it is

observed that the oxidation current of formic acid at 3600 s is 0.26, 5.50, 3.14 and 3.83 mA mg^{-1}_{Pd}, respectively. Here, compared with the undoped N catalyst Pd/Coal-CFs, the oxidation peak potential of the N-doped catalyst shifted to a negative direction of about 0.085 V, and the N doped catalyst showed better performance than that of the undoped N catalyst. Moreover the rule of amperometric i-t curve is consistent with CV test. Combined with the conclusions of these two tests, we can draw a conclusion that N doped coal-based CFs Pd catalyst is more favorable for formic acid oxidation than that of undoped N coal-based CFs Pd catalyst. The above results demonstrate that the formic acid oxidation activity and electrocatalytic stability of Pd/N-Coal-CFs(DCD) catalyst is obviously superior to those of other N doped catalysts. Figure S3C and Figure S3D show the cyclic voltammograms and electrocatalytic stabilities of the Coal-CFs, P-Coal-CFs(TPP), P-Coal-CFs(NaH_2PO_4) and P-Coal-CFs(H_3PO_4) catalyst electrodes at the same conditions as above. The specific oxidative mass activity of Pd/Coal-CFs, Pd/P-Coal-CFs(H_3PO_4), Pd/P-Coal-CFs(NaH_2PO_4) and Pd/P-Coal-CFs(TPP) catalyst electrodes is determined as 214.3, 251.8, 316.3 and 470.9 mA mg^{-1}_{Pd}, respectively. The corresponding mass activity of electrocatalytic stability of these catalysts at 3600 s is 0.26, 1.86, 2.37 and 5.58 mA mg^{-1}_{Pd}, respectively. This proves that Pd/CF catalyst with P source of TPP has much higher electrochemical activity and stability than that of other two P source doped catalysts and undoped P catalyst. Therefore, DCD and TPP as N source and P source dual-doped catalyst Pd/NP-Coal-CFs(DCD/TPP) was carried out a detailed electrochemical test.

Table S5. Comparison of Pd content and electrochemical catalytic analysis

Sample	Pd wt %[a]	ECSA[b] (m^2/g)	ECSA[c] (m^2/g)	Onset potential of CO_{ads}[d] (V)	Current density[e] (mA mg^{-1} $_{Pd}$)		L_{Pd} [f] (mg)
					Forward	Backward	
Pd/Coal-CFs	19.79%	30.40	43.99	0.79	214.3	188.9	0.00494750
Pd/N-Coal-CFs(DCD)	14.95%	42.21	52.95	0.77	450.0	307.6	0.00372255
Pd/P-Coal-CFs(TPP)	18.24%	42.60	86.96	0.74	470.9	412.6	0.00461472
Pd/NP-Coal-CFs(DCD/TPP)	17.98%	87.84	88.67	0.72	536.6	479.5	0.00449500

[a]Pd wt. %: Pd content calculated from ICP detection.

[b] ECSA: ECSA calculated from the hydrogen desorption area of the CV curves in 0.5 mol L^{-1} H_2SO_4.

[c] ECSA: ECSA of the catalysts integration from the. CO_{ads} stripping experiment.

[d] Onset potential of CO_{ads}: Onset potential of CO_{ads} from the anode peaks of the CO stripping curves.

[e] Current density: Current density from the forward and backward peaks from the CV of formic acid oxidation.

[f] L_{Pd}/mg: Actual Pd content at the working electrode.

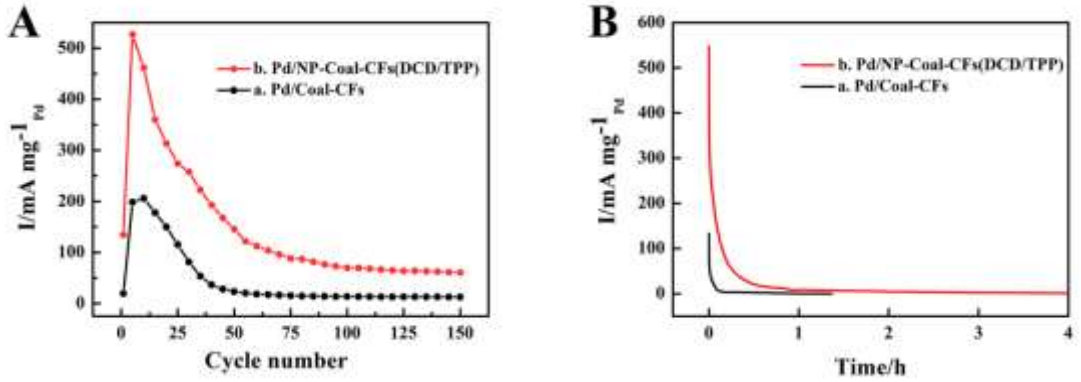

Figure S4. (A) The current density of CVs versus cycle number; (B) Amperometric i-t curves of (a) Pd/Coal-CFs; (b) Pd/NP-Coal-CFs(DCD/TPP)

REFERENCES

(1) Guo, M.; Guo, J.; Jia, D.; Zhao, H.; Sun, Z.; Song, X.; Li, Y. Coal Derived Porous Carbon Fibers with Tunable Internal Channels for Flexible Electrodes and Organic Matter Absorption. *J. Mater. Chem. A* **2015,** *3*, 21178–21184.

(2) Zhao, H.; Wang, L.; Jia, D.; Xia, W.; Li, J.; Guo, Z. Coal Based Activated Carbon Nanofibers Prepared by Electrospinning. *J. Mater. Chem. A* **2014,** *2*, 9338–9344.