

Electronic Supplementary Information

In-situ self-doped biomass-derived porous carbon as excellent oxygen reduction electrocatalyst for fuel cell and metal-air battery

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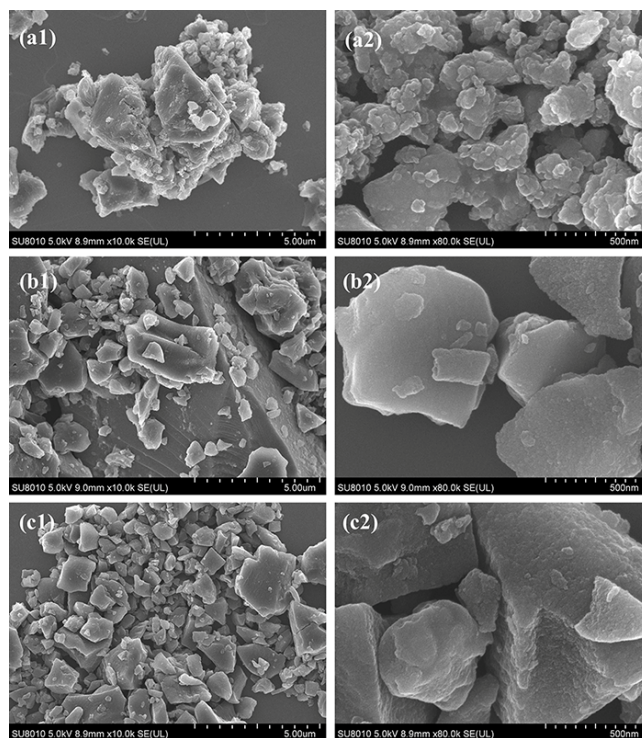


Fig. S1 SEM images of as-prepared catalysts at various temperatures: (a1-a2) RN350-1000; (b1-b2) RN350-Z(1-2)-700; (c1-c2) RN350-Z(1-2)-800.

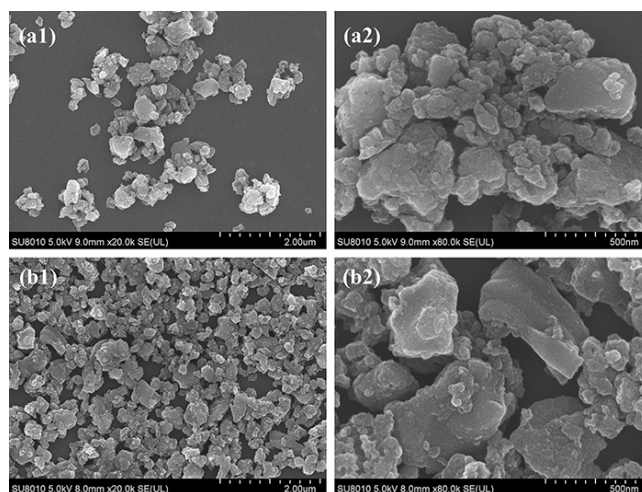


Fig. S2 SEM images of (a1-a2) RN350-Z(1-2)-900; (b1-b2) RN350-Z(1-2)-1000.

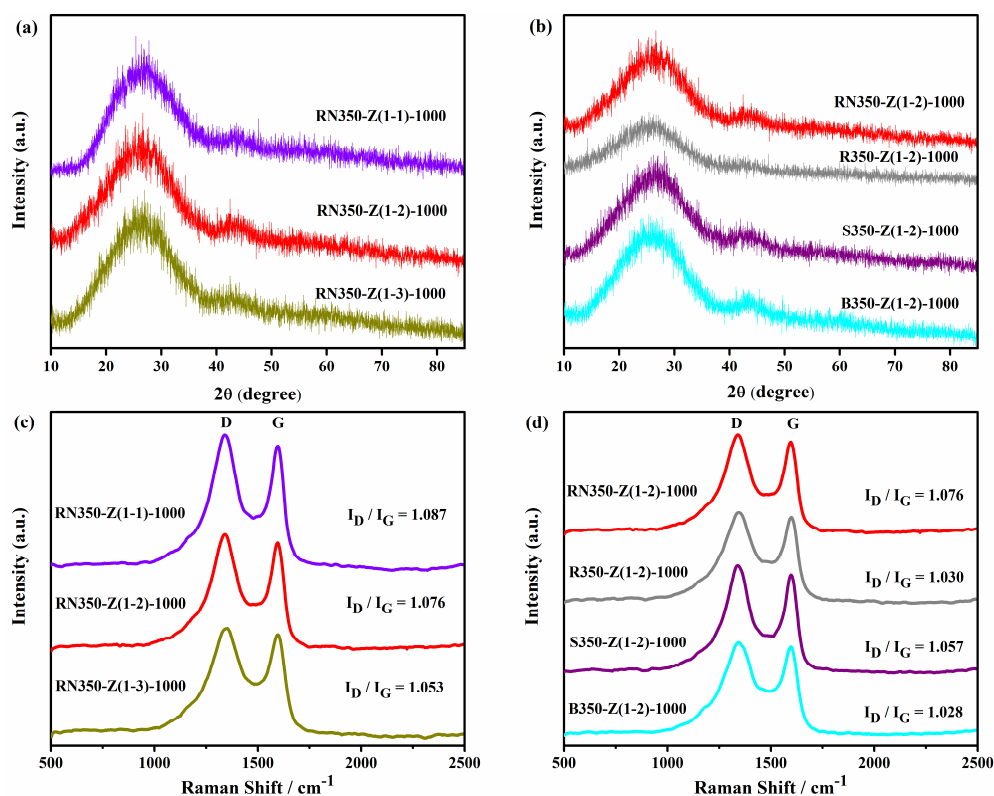


Fig. S3 (a) XRD pattern of RN350-Z(1-x)-1000 ($x = 1, 2, 3$). (b) XRD pattern of RN350-Z(1-2)-1000, R350-Z(1-2)-1000, S350-Z(1-2)-1000, and B350-Z(1-2)-1000. (c) Raman spectra of RN350-Z(1-x)-1000 with the corresponding I_D/I_G values. (d) Raman spectra of RN350-Z(1-2)-1000, R350-Z(1-2)-1000, S350-Z(1-2)-1000, and B350-Z(1-2)-1000 with the corresponding I_D/I_G values.

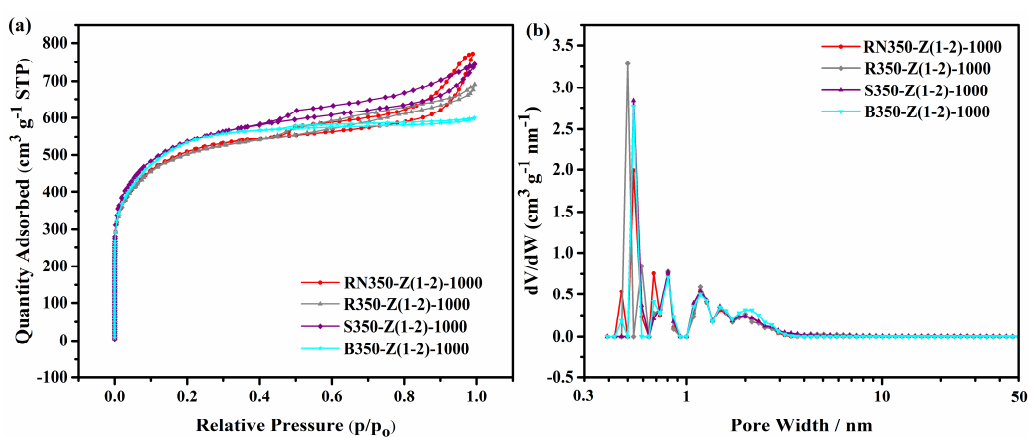


Fig. S4 (a) N_2 adsorption-desorption isotherms of RN350-Z(1-2)-1000, R350-Z(1-2)-1000, S350-Z(1-2)-1000, and B350-Z(1-2)-1000. (b) The corresponding pore size distributions.

Table S1. Textural properties of RN350-1000, RN350-Z(1-2)-T (T = 700, 800, 900, and 1000 °C).

Sample	S ^a _{BET} (m ² /g)	S ^b _{micro} (m ² /g)	S _{meso} (m ² /g)	V ^c _{total} (cm ³ /g)	V ^d _{micro} (cm ³ /g)	V _{meso} (cm ³ /g)	Pore size ^e (nm)	
							Micro ^f (nm)	D _{av} ^g (nm)
RN350-1000	440.13	192.01	248.12	0.3302	0.0823	0.2479	0.5538	3.00
RN350-Z(1-2)-700	1550.31	1106.43	443.88	0.7076	0.4558	0.2518	0.6016	1.83
RN350-Z(1-2)-800	1542.13	1010.23	531.90	0.7171	0.4246	0.2925	0.6012	1.86
RN350-Z(1-2)-900	1537.97	696.34	841.63	0.9402	0.2940	0.6462	0.6191	2.45
RN350-Z(1-2)-1000	1835.08	886.02	949.06	1.1942	0.3629	0.8313	0.6136	2.60

^a Surface area determined by the BET method.

^b Micropore surface area determined by t-Plot micropore area.

^c Total pore volume calculated by the DFT method.

^d Micropore volume determined by t-Plot micropore volume.

^e the pore distribution curves determined by the DFT method.

^f Micropore width determined by the HK method.

^g Average pore width determined by adsorption average pore width (4V/A by BET).

Table S2. Textural properties of RN350-Z(1-2)-1000, R350-Z(1-2)-1000, S350-Z(1-2)-1000, and B350-Z(1-2)-1000.

Sample	S _{BET} (m ² /g)	S _{micro} (m ² /g)	S _{meso} (m ² /g)	V _{total} (cm ³ /g)	V _{micro} (cm ³ /g)	V _{meso} (cm ³ /g)	Pore size (nm)	
							Micro (nm)	D _{av} (nm)
RN350-Z(1-2)-1000	1835.08	886.02	949.06	1.1942	0.3629	0.8313	0.6136	2.60
R350-Z(1-2)-1000	1794.18	887.07	907.11	1.0695	0.3723	0.6972	0.6101	2.38
S350-Z(1-2)-1000	1946.26	907.94	1038.32	1.1512	0.3680	0.7832	0.6167	2.37
B350-Z(1-2)-1000	1901.23	749.68	1151.55	0.9276	0.3109	0.6167	0.6149	1.95

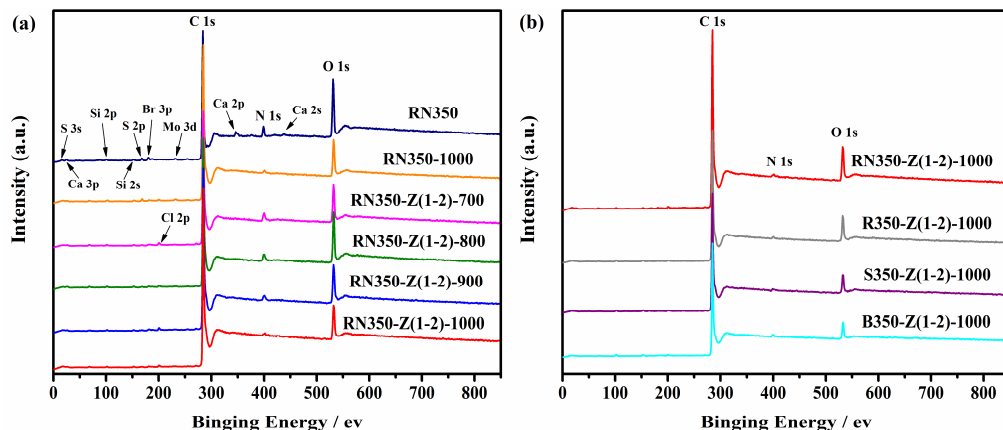


Fig. S5 (a) The full XPS spectra of RN350, RN350-1000, and RN350-Z(1-2)-T (T = 700, 800, 900, and 1000 °C). (b) The full XPS spectra of RN350-Z(1-2)-1000, R350-Z(1-2)-1000, S350-Z(1-2)-1000, and B350-Z(1-2)-1000.

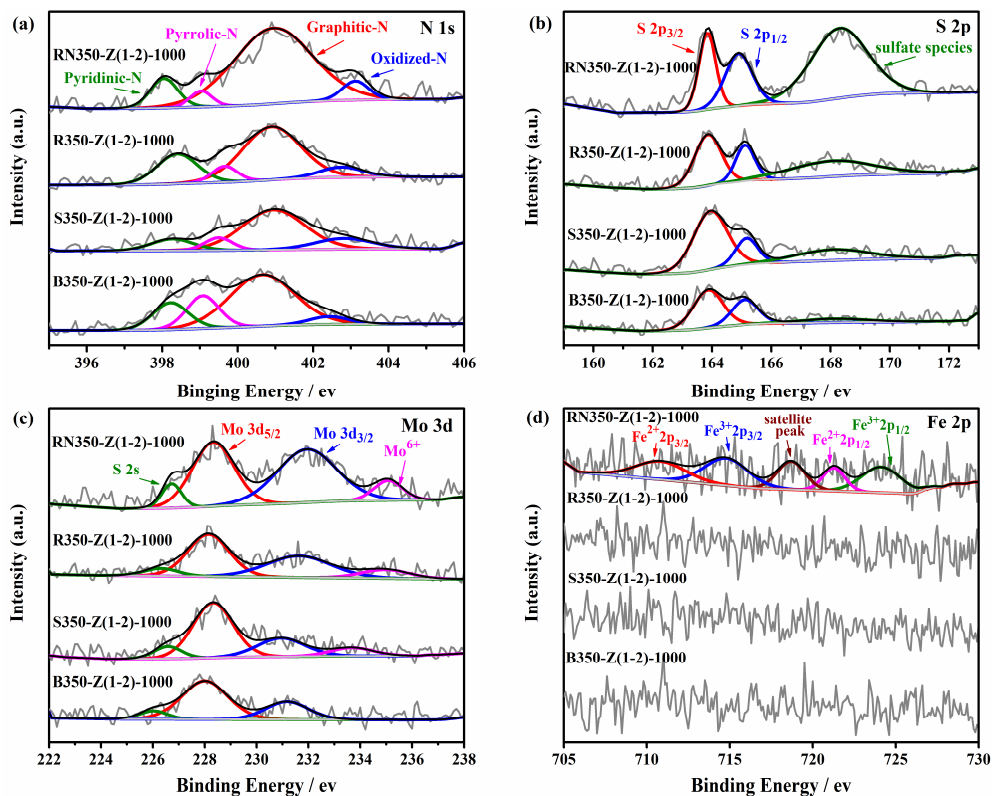


Fig. S6 (a) High-resolution N 1s spectra of RN350-Z(1-2)-1000, R350-Z(1-2)-1000, S350-Z(1-2)-1000, and B350-Z(1-2)-1000. (b) High-resolution S 2s spectra. (c) High-resolution Mo 3d spectra. (d) High-resolution Fe 2p spectra.

Table S3. Elemental compositions of RN350, RN350-1000, RN350-Z(1-2)-T (T = 700, 800, 900, and 1000 °C), RN350-HF and RN350-HF-Z(1-2)-1000 calculated by XPS dates.

Sample	C (at %)	N (at %)	O (at %)	S (at %)	Mo (at %)	Fe (at %)	N-1 % (at %)	N-2 % (at %)	N-3 % (at %)	N-4 % (at %)
RN350	78.45	4.51	16.12	0.81	0.11	*	-	-	-	-
RN350-1000	87.21	1.50	10.28	0.90	0.11	*	15.22 (0.229)	7.76 (0.116)	71.53 (1.073)	5.49 (0.082)
RN350-Z(1-2)-700	84.07	4.50	11.09	0.30	0.04	*	22.22 (1.000)	7.92 (0.356)	66.03 (2.972)	3.83 (0.172)
RN350-Z(1-2)-800	82.28	3.64	13.73	0.31	0.04	*	23.71 (0.863)	10.45 (0.380)	59.92 (2.181)	5.92 (0.216)
RN350-Z(1-2)-900	86.20	2.80	10.49	0.45	0.06	*	17.32 (0.485)	9.86 (0.276)	66.51 (1.862)	6.31 (0.177)
RN350-Z(1-2)-1000	88.94	1.45	9.20	0.36	0.05	*	10.69 (0.155)	4.65 (0.067)	77.99 (1.131)	6.67 (0.097)
RN350-HF	81.42	5.28	13.12	0.16	0.02	*	-	-	-	-
RN350-HF-Z(1-2)-1000	88.81	1.90	8.86	0.39	0.05	*	19.47 (0.370)	4.71 (0.089)	68.68 (1.305)	7.15 (0.136)

N-1: Pyridinic-N; N-2: Pyrrolic-N; N-3: Graphitic-N; N-4: Oxidized-N.

* Due to the content of Fe element is very small, the peak intensity of all high-resolution Fe 2p spectra are slight, which calculated by integrated area has a great error, therefore, the content of Fe element that calculated by XPS is negligible.

Table S4. Elemental compositions of RN350-Z(1-2)-1000, R350-Z(1-2)-1000, S350-Z(1-2)-1000, and B350-Z(1-2)-1000 calculated by XPS dates.

Sample	C (at %)	N (at %)	O (at %)	S (at %)	Mo (at %)	Fe (at %)	N-1 % (at %)	N-2 % (at %)	N-3 % (at %)	N-4 % (at %)
RN350-Z(1-2)-1000	88.94	1.45	9.20	0.36	0.05	*	10.69 (0.155)	4.65 (0.067)	77.99 (1.131)	6.67 (0.097)
R350-Z(1-2)-1000	89.21	1.46	9.06	0.24	0.04	*	23.63 (0.345)	8.03 (0.117)	59.70 (0.872)	8.65 (0.126)
S350-Z(1-2)-1000	90.80	1.28	7.57	0.30	0.05	*	12.40 (0.159)	8.85 (0.113)	63.01 (0.807)	15.74 (0.201)
B350-Z(1-2)-1000	91.23	1.80	6.75	0.19	0.04	*	16.92 (0.305)	18.89 (0.340)	58.57 (1.054)	5.61 (0.101)

Table S5. The content of C, N, H, and S for as-prepared samples were analyzed by elemental analysis (EA) measurement and the content of Mo and Fe were analyzed by inductive coupled plasma emission spectrometer (ICP) measurement.

Sample	EA mass ratio (%)				ICP mass ratio (%)	
	C	N	H	S	Mo	Fe
RN350	63.60 / 63.65	5.13 / 5.12	4.37 / 4.35	0.76 / 0.54	0.0067	0.034
RN350-1000	76.44 / 76.90	1.26 / 1.28	1.42 / 1.48	<0.3	0.0010	0.017
RN350-Z(1-2)-700	68.95 / 69.11	4.82 / 4.81	3.08 / 3.07	0.40 / 0.39	0.0013	0.038
RN350-Z(1-2)-800	72.72 / 72.50	4.68 / 4.66	2.85 / 2.53	0.47 / 0.46	0.0017	0.0301
RN350-Z(1-2)-900	74.54 / 74.71	2.63 / 2.68	2.98 / 3.02	0.54 / 0.52	0.056	0.101
RN350-Z(1-2)-1000	63.37 / 64.83	1.25 / 1.27	2.30 / 2.35	0.37 / 0.40	0.031	0.106
RN350-HF-Z(1-2)-1000	62.58 / 62.86	1.51 / 1.59	2.31 / 2.04	0.60 / 0.55	0.0011	0.02

Table S6. The content of C, N, H, and S were analyzed by elemental analysis (EA) measurement, and the content of Mo and Fe were analyzed by inductive coupled plasma emission spectrometer (ICP) measurement.

Sample	EA mass ratio (%)				ICP mass ratio (%)	
	C	N	H	S	Mo	Fe
RN350-Z(1-2)-1000	63.37 / 64.83	1.25 / 1.27	2.30 / 2.35	0.37 / 0.40	0.031	0.106
R350-Z(1-2)-1000	81.66 / 81.58	1.38 / 1.35	3.10 / 3.24	0.32 / 0.32	0.0225	0.0401
S350-Z(1-2)-1000	84.34 / 84.48	0.90 / 0.92	2.85 / 2.76	0.41 / 0.42	0.0058	0.0248
B350-Z(1-2)-1000	76.52 / 76.39	1.54 / 1.50	1.27 / 1.14	0.45 / 0.49	0.0114	0.042

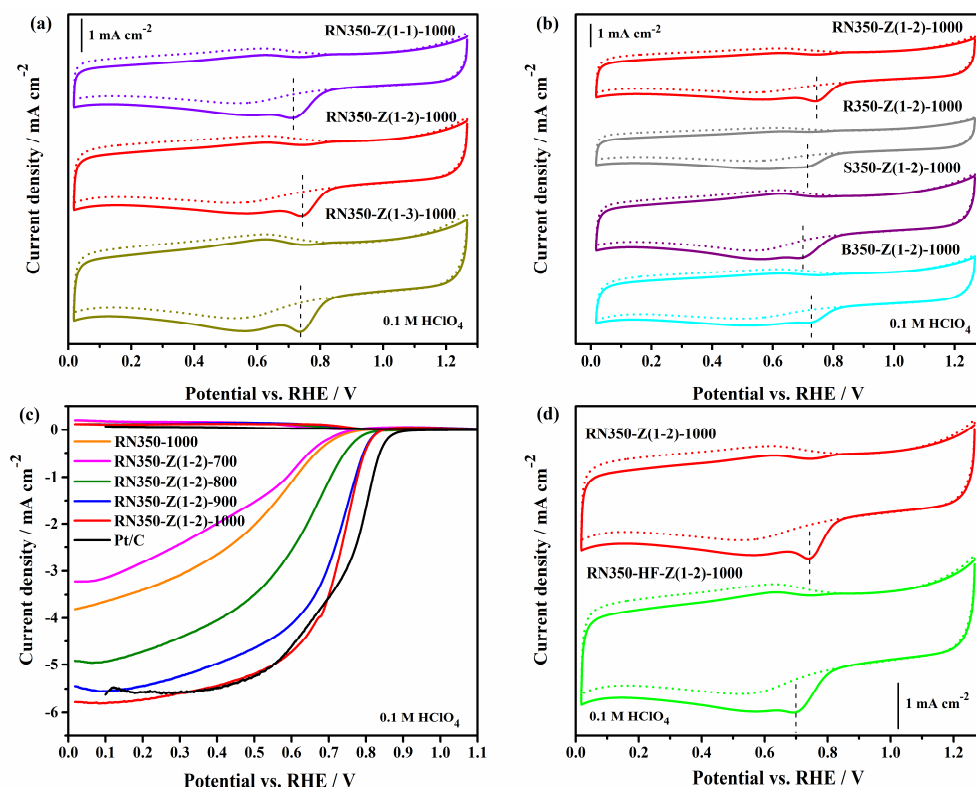


Fig. S7 (a) CV curves of RN350-Z(1-x)-1000 (x = 1, 2, 3) in O₂ or N₂-saturated 0.1 M HClO₄ solution at a scan rate of 10 mV s⁻¹. (b) CV curves of RN350-Z(1-2)-1000, R350-Z(1-2)-1000, S350-Z(1-2)-1000, and B350-Z(1-2)-1000 in 0.1 M HClO₄ solution. (c) Rotating ring disk electrode (RRDE) curves of as-prepared catalysts and Pt/C in O₂-saturated 0.1 M HClO₄ solution at a rate of 10 mV s⁻¹ and a rotating rate of 1600 rpm. (d) CV curves of RN350-Z(1-2)-1000 and RN350-HF-Z(1-2)-1000 in O₂ or N₂-saturated 0.1 M HClO₄ solution.

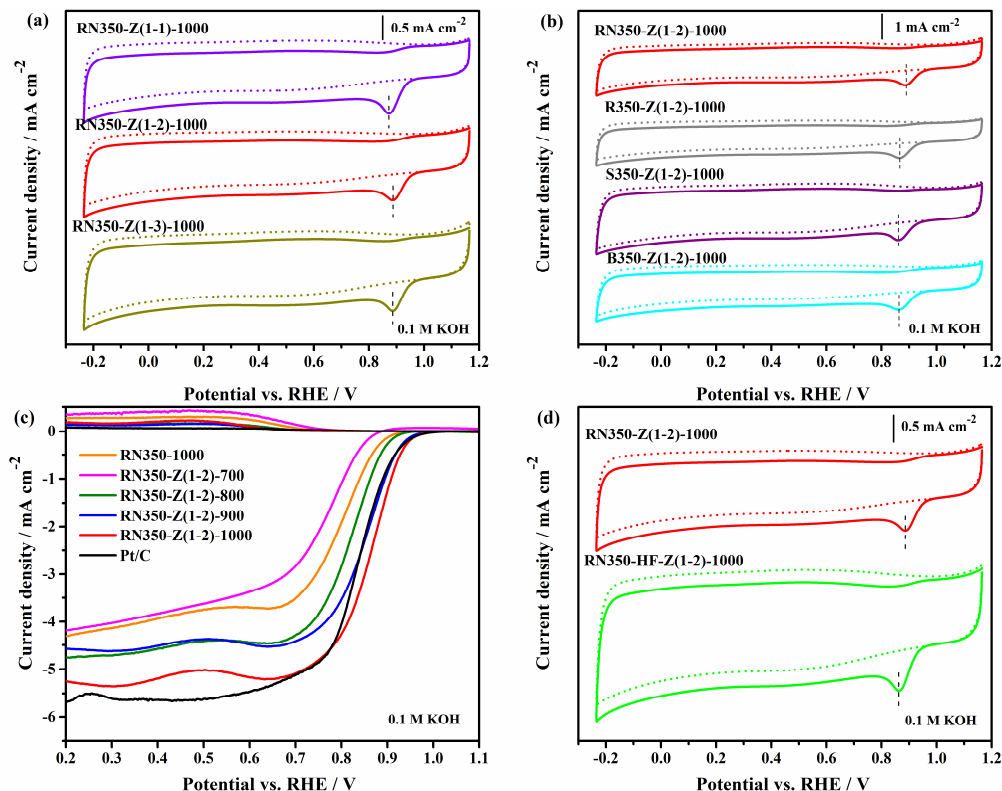


Fig. S8 (a) CV curves of RN350-Z(1-x)-1000 (x = 1, 2, 3) in O₂ or N₂-saturated 0.1 M KOH solution at a scan rate of 10 mV s⁻¹. (b) CV curves of RN350-Z(1-2)-1000, R350-Z(1-2)-1000, S350-Z(1-2)-1000, and B350-Z(1-2)-1000 in 0.1 M KOH solution. (c) Rotating ring disk electrode (RRDE) curves of as-prepared catalysts and Pt/C in O₂-saturated 0.1 M KOH solution at a rate of 10 mV s⁻¹ and a rotating rate of 1600 rpm. (d) CV curves of RN350-Z(1-2)-1000 and RN350-HF-Z(1-2)-1000 in O₂ or N₂-saturated 0.1 M KOH solution.

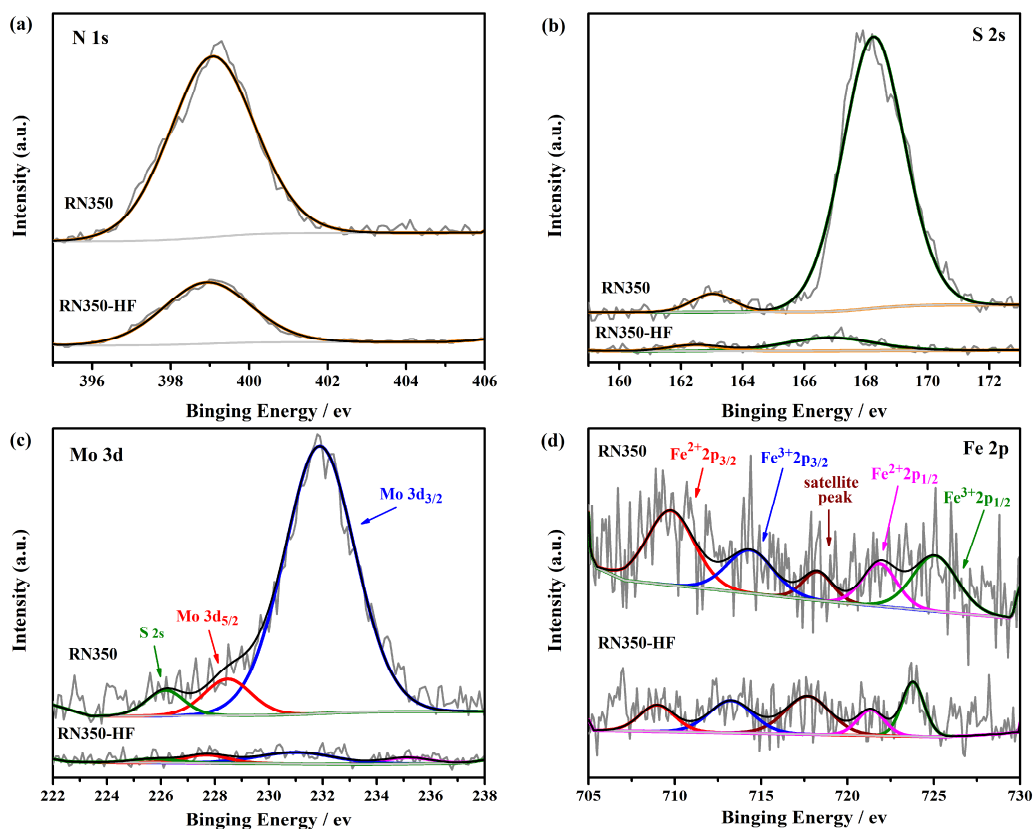


Fig. S9 (a) High-resolution N 1s spectra of RN350 and RN350-HF. (b) High-resolution S 2s spectra. (c) High-resolution Mo 3d spectra. (d) High-resolution Fe 2p spectra.

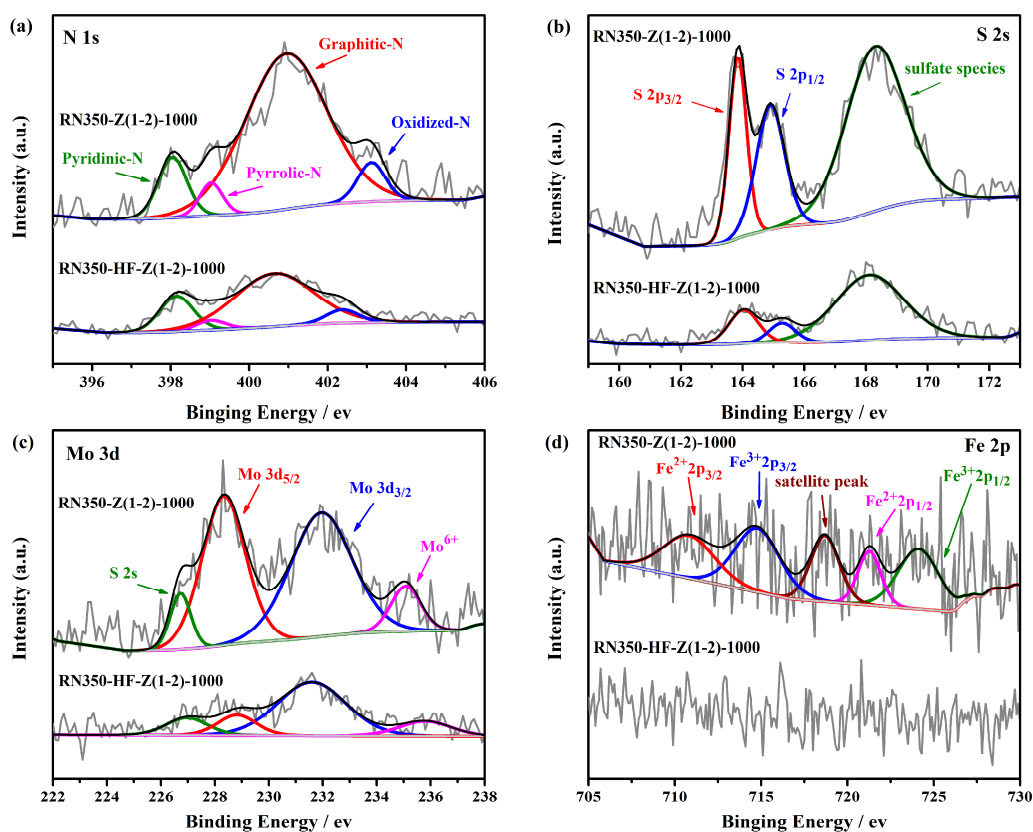


Fig. S10 (a) High-resolution N 1s spectra of RN350-Z(1-2)-1000 and RN350-HF-Z(1-2)-1000. (b) High-resolution S 2s spectra. (c) High-resolution Mo 3d spectra. (d) High-resolution Fe 2p spectra.

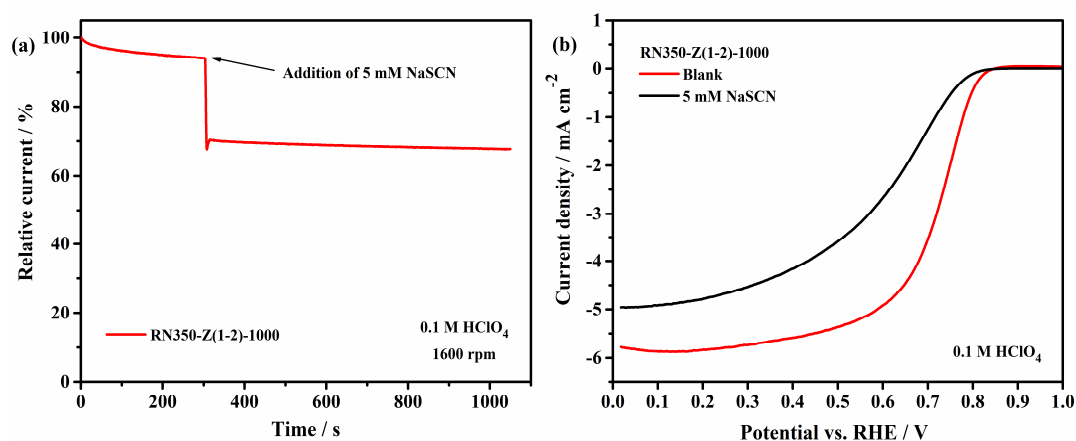


Fig. S11 (a) Current-time curves of the RN350-Z(1-2)-1000 in O_2 -saturated 0.1 M $HClO_4$ solution at 0.6 V while 5 mM NaSCN was added at 300 s; (b) LSV curves of electrocatalyst RN350-Z(1-2)-1000 with and without 5 mM NaSCN.

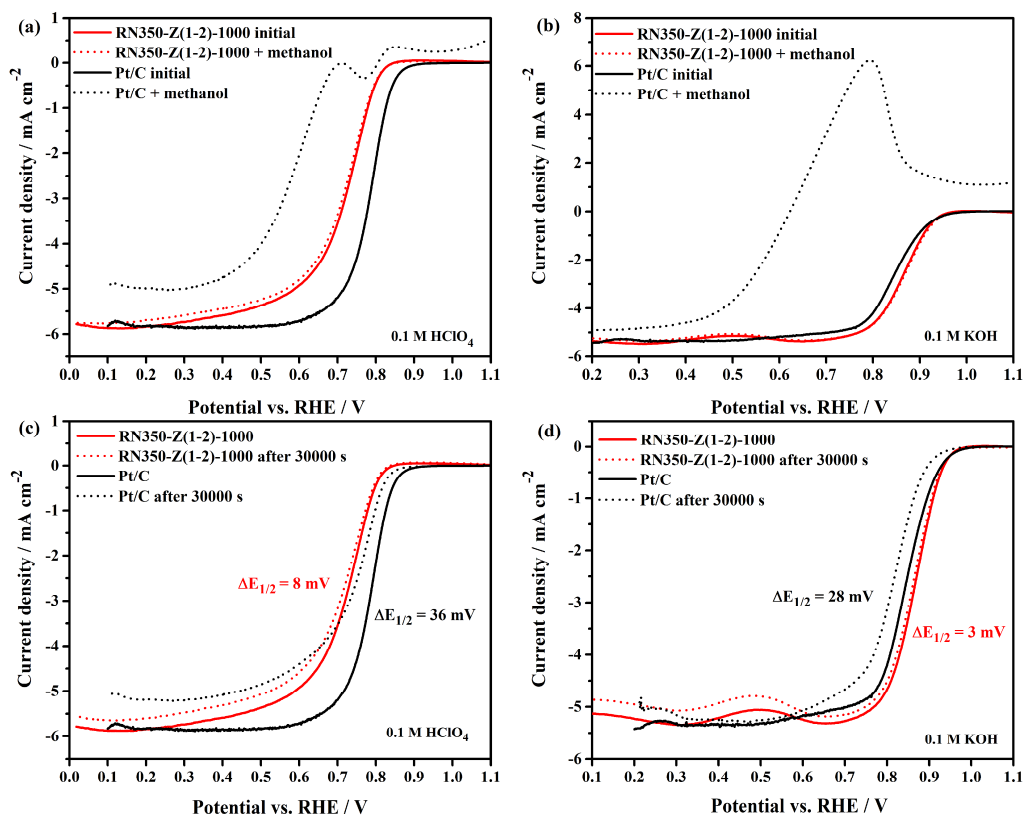


Fig. S12 (a) LSV curves of RN350-Z(1-2)-1000 and Pt/C in O₂-saturated 0.1 M HClO₄ solution at a rotating rate of 1600 rpm with/without 1 M methanol. (b) LSV curves of RN350-Z(1-2)-1000 and Pt/C in O₂-saturated 0.1 M KOH solution with/without 1 M methanol. (c) LSV curves of RN350-Z(1-2)-1000 and Pt/C before and after 30000 s durability measurement in O₂-saturated 0.1 M HClO₄ solution. (d) LSV curves of RN350-Z(1-2)-1000 and Pt/C before and after 30000 s durability measurement in O₂-saturated 0.1 M KOH solution.

Table S7. The detailed biomass resources and synthesis conditions of each electrocatalysts. The heating rate of all samples is 5 °C min⁻¹, and keep at maximum temperature for 2 hours.

Sample	Resource	Precursor	ZnCl ₂	Mass ratio of Precursor/ZnCl ₂	Heating Temperature (°C)
RN350	Root nodules	-	-	-	350
RN350-1000	Root nodules	RN350	-	-	1000
RN350-Z(1-2)-700	Root nodules	RN350 (450 mg)	900 mg	1:2	700
RN350-Z(1-2)-800	Root nodules	RN350 (450 mg)	900 mg	1:2	800
RN350-Z(1-2)-900	Root nodules	RN350 (450 mg)	900 mg	1:2	900
RN350-Z(1-2)-1000	Root nodules	RN350 (450 mg)	900 mg	1:2	1000
RN350-Z(1-1)-1000	Root nodules	RN350 (450 mg)	450 mg	1:1	1000
RN350-Z(1-3)-1000	Root nodules	RN350 (450 mg)	1350 mg	1:3	1000
R350	Root	-	-	-	350
R350-Z(1-2)-1000	Root	R350 (450 mg)	900 mg	1:2	1000
S350	Stem	-	-	-	350
S350-Z(1-2)-1000	Stem	S350 (450 mg)	900 mg	1:2	1000
B350	Beans	-	-	-	350
B350-Z(1-2)-1000	Beans	B350 (450 mg)	900 mg	1:2	1000
RN350-HF	Root nodules	RN350	-	-	-
RN350-HF-Z(1-2)-1000	Root nodules	RN350-HF (450 mg)	900 mg	1:2	1000

Table S8. Comparison of biomass sources, synthesis strategies, BET area and ORR performance from this work and recent research reported biomass-derived ORR electrocatalysts in acidic and alkaline medium.

Biomass source	Heteroatom precursors	Other precursors	Synthesis strategy	Surface area [m ² g ⁻¹]	Electrolyte	E _{onset} [V] (1600 rpm)	E _{1/2} [V]	J _L [mA cm ⁻²]	Reference
Legume root nodules	Self-doping (N、S)	ZnCl ₂ , self-doping (Fe、Mo)	Precarbonization, activation, pyrolysis in Ar	1835	0.1 M HClO ₄	0.827	0.723	5.78	This work
					0.1 M KOH	0.970	0.868	5.23	
Commercial Pt/C (20 %)					0.1 M HClO ₄	0.882	0.785	5.83	This work
					0.1 M KOH	0.963	0.843	5.34	
Enoki Mushroom	Self-doping (N)	Carbon nanotubes	Ball-milling, pyrolysis in N ₂	305.3	0.1 M HClO ₄	0.81	0.60	2.85	S ¹
					0.1 M KOH	0.94	0.81	3.98	
Cellulose	2-methylimidazole (N)	Co (NO ₃) ₂	MOF growth, Freeze drying, pyrolysis in N ₂	235.7	0.5 M H ₂ SO ₄	0.827	0.634	6.45	S ²
					0.1 M KOH	0.952	0.852	6.4	
Bacterial cellulose	NH ₃ (N)	-	Freeze drying, pyrolysis in N ₂ , second pyrolysis in NH ₃	916	0.1 M KOH	-	0.80	5.2	S ³
Spinach leaves	Self-doping (N、P、S)	ZnCl ₂	Activation, pyrolysis in Ar	1145	0.1 M KOH	0.95	0.82	5.19	S ⁴
Fructus azedarach	H ₃ PO ₄ , NH ₄ H ₂ PO ₄ (N、P)	KHCO ₃	Smash, hydrothermal, activation, pyrolysis in N ₂	1584	0.1 M KOH	0.94	0.84	6.01	S ⁵
Corn silks	NH ₃ (N), Self-doping (P)	FeCl ₃	Hydrothermal carbonization, pyrolysis in NH ₃ , doped FeCl ₃ , pyrolysis in NH ₃	1038.9	0.1 M KOH	0.957	0.852	5.6	S ⁶
Egg	NH ₃ ·H ₂ O (N), self-doping (P)	Si (OEt) ₄ , KOH, self-doping (Fe)	Hydrolysis, spray-dry, carbonization in N ₂ , silica etching	970	0.1 M KOH	0.84	0.69	4.36	S ⁷
Chicken feathers	NH ₃ (N) Self-doping (S)	KOH	Precarbonized KOH activation, Pyrolysis in N ₂ +NH ₃	1098	0.1 M KOH	0.948	0.835	5.33	S ⁸

Chicken manure	Hydrazine (N), H ₃ PO ₄ (P)	KOH	Carbonized in Ar, KOH activation, Pyrolysis in Ar, mixing H ₃ PO ₄ , pyrolysis, activated in hydrazine	512.2	0.1 M KOH	0.86	0.80	3.94	S ⁹
Cystine	NH ₃ (N), Self-doping (S)	KOH	Precarbonization, Pyrolysis in Ar, acid washing, pyrolysis in NH ₃	1309	0.1 M HClO ₄	0.809	0.609	6.0	S ¹⁰
					0.1 M KOH	0.953	0.849	5.7	
Coconut palm leaves	Melamine (N)	KOH, KHCO ₃	Carbonization, activation, pyrolysis in N ₂	1419.08	0.5 M H ₂ SO ₄	0.84	0.66	4.97	S ¹¹
					0.1 M KOH	1.01	0.87	5.5	
Typha orientalis	NH ₃ (N)	-	Hydrothermal process, freeze drying, pyrolysis in NH ₃	646	0.5 M H ₂ SO ₄	0.725	-	3.3	S ¹²
Bamboo stems	Thiourea (N, S)	-	Carbonization, steam activated, mixed with thiourea, pyrolysis in Ar	349.1	0.1 M KOH	-	0.85	4.14	S ¹³
Kelps	Self-doping (N, S, P)	Co(NO ₃) ₂ ·6 H ₂ O	Pyrolysis in N ₂	141.7	0.1 M KOH	0.90	0.74	5.5	S ¹⁴
Reed	1, 10-phen (N)	KOH, Fe (Ac) ₂	Carbonization, activation, pyrolysis in Ar	534.9	0.1 M KOH	1.00	0.88	5.2	S ¹⁵
Porphyra	Self-doping (N)	KOH, Hemin (Fe)	Activation, carbonization, absorption, pyrolysis in Ar	1499.1	0.1 M KOH	-	0.87	5.0	S ¹⁶
Water hyacinth	Self-doping (N)	ZnCl ₂	Activation, Pyrolysis in N ₂	950.6	0.1 M KOH	0.98	-	4.15	S ¹⁷
Willow catkins	NH ₃ (N)	Cobalt (II) acetylacetonate	Pyrolysis, doped Co, pyrolysis in Ar-NH ₃	470.1	0.1 M KOH	0.906	0.778	4.5	S ¹⁸
Soybean milk	Self-doping (N)	FeCl ₃	freeze drying, pyrolysis in N ₂	1247	0.1 M NaOH	0.91	0.821	4.5	S ¹⁹
Chlorella	Melamine (N)	Co (Ac) ₂	Pyrolysis in Ar	728	0.1 M KOH	-	0.87	5.0	S ²⁰
Chitosan	NH ₄ Cl (N)	-	freeze drying, pyrolysis in Ar	1005	0.1 M KOH	1.017	0.861	5.2	S ²¹

Chitosan	Self-doping (N)	Zn (NO ₃) ₂	Pyrolysis in N ₂	794.7	0.1 M KOH	0.96	0.86	6.7	S ²²
Chitosan	Vitamin B12 (N, Co), NH ₄ OH (N)	SiO ₂ , Heme (Fe)	Polymerization, Pyrolysis in N ₂ , HF etching-off SiO ₂	225.2	0.1 M HClO ₄	-	0.70	5.7	S ²³
					0.1 M KOH	-	0.84	5.5	
Cotton fibers	NH ₄ Cl (N)	-	Pyrolysis in N ₂	912.1	0.1 M KOH	0.981	0.82	5.286	S ²⁴
Silk cocoon	Thiourea (N)	KOH	Pyrolysis in N ₂	377	0.1 M KOH	0.853	0.717	4.5	S ²⁵
cocoon	Self-doping (N, S)	Na ₂ CO ₃ , CaCl ₂ , FeCl ₃	Washing with Na ₂ CO ₃ solution, washing with CaCl ₂ solution, mixing with FeCl ₃ , freeze-drying, pyrolysis in N ₂	714.4	0.1 M KOH	0.94	0.79	3.8	S ²⁶
Glucose	Thiourea (N, S)	Co (NO ₃) ₂	Polymerization, impregnation, pyrolysis in N ₂	667	0.1 M KOH	0.946	0.821	5.5	S ²⁷
Seaweed	Carbon nanotubes, NH ₃ (N)	CoCl ₂ , NiCl ₂	Freeze-drying, Pyrolysis in NH ₃	193	0.1 M KOH	0.89	0.74	4.9	S ²⁸
Lignin	HNO ₃ , H ₂ SO ₄ , nitration (N)	KCl, ZnCl ₂	Extraction, aromatic nitration, Pyrolysis in N ₂	1589	0.1 M KOH	-	0.85	4.6	S ²⁹
Pork hearts	Self-doping (N)	KOH	Freeze drying, carbonization, activation, pyrolysis in Ar	1718.84	0.1 M KOH	0.92	0.80	-	S ³⁰
Cattle bone	Vitamin B12 (N, Co)	KOH	Precarbonization, activation, pyrolysis in Ar, impregnation, pyrolysis in Ar	2520	0.1 M KOH	-	0.835	5.2	S ³¹
Cattle bone	Phytic acid (P) Dicyandiamide (N)	KOH	Precarbonization, activation, pyrolysis in Ar, mixing with PA and DCDA, pyrolysis in Ar	1516	0.1 M KOH	-	0.853	-	S ³²

Walnut shells	NH ₃ (N)	FeCl ₃	Pyrolysis in NH ₃	714.06	0.1 M KOH	0.847	0.773	5.987	S ³³
Peanut shells	Self-doping (N)	Co (OH) ₂ (Co) NaH ₂ PO ₂ (P)	Pyrolysis in N ₂ , activated in CO ₂	671.4	0.5 M H ₂ SO ₄	0.89	0.68	3.26	S ³⁴
					0.1 M KOH	0.91	0.81	5.7	
Keratin	Self-doping (S) NH ₃ (N)	KOH	Precarbonized, activation, pyrolysis in N ₂ , acid-washing, pyrolysis in N ₂ +NH ₃	1799	0.1 M KOH	0.971	0.842	-	S ³⁵
Tea leaf residual	Self-doping (N, F)	-	Pyrolysis in N ₂	855.6	0.1 M KOH	0.81	0.66	5.1	S ³⁶

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