Supplementary Information

Nitrogen doped porous activated carbon derived from cocoon silk as highly efficient metal-free electrocatalyst for oxygen reduction reaction

Peng Fu,[a] Lihua Zhou,*[a] Lihua Sun,[a] Baohua Huang,[a] and Yong Yuan,**[b]

[a] Institute of Natural Medicine and Green Chemistry, School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou, 510006, P.R. China.

[b] Guangdong Key Laboratory of Integrated Agro-environmental Pollution Control and Management, Guangdong Institute of Eco-Environmental Science and Technology, 510650, P.R. China.

***Corresponding author:**

E-mail: qhzhoulh@gdut.edu.cn (L. Zhou); Tel: +8620-39322203

E-mail: yuanyong@soil.gd.cn (Y. Yuan); Tel: +8620-87025872

Table S1 Summary of textural parameters obtained from nitrogen adsorption analysis of these samples

Samples	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
PAC-600	983.9	0.47	1.8
PAC -700	1102.3	0.50	1.8
PAC -800	1273.8	0.60	1.9
PAC -900	1059.4	0.46	1.8
DC -800	136.97	0.06	1.9

Table S2 XRD results of the CS-derived carbon nanofibers

Samples	2θ/°	$d_{(002)}$/nm	$L_{c(002)}$ /nm	$L_{a(101)}$ /nm	N ($L_{c(002)}$/ $d_{(002)}$)
PAC-600	24.62	0.3612	1.81	2.12	5.01
PAC -700	24.67	0.3606	1.86	2.68	5.17
PAC -800	24.73	0.3597	1.93	2.97	5.45
PAC -900	24.75	0.3594	1.97	3.13	5.48
DC -800	24.72	0.3598	2.11	3.37	5.86

Table S3 N functionalities in the porous carbons determined by XPS measurements

Samples	Pyridinic–N1 (at.%)	Pyrrolic–N2 (at.%)	Graphitic–N3 (at.%)	Oxidized–N4 (at.%)	Total Nitrogen (at.%)
PAC-600	3.13	2.42	4.02	2.52	**12.09**
PAC -700	1.69	1.47	3.99	2.42	**9.39**
PAC -800	0.91	0.86	4.04	1.69	**7.49**
PAC -900	0.88	0.78	3.68	1.52	**6.86**
DC -800	0.91	1.06	3.85	1.57	**7.39**

Table S4 Summary of the reported ORR performance of various biomass-derived metal-free activated carbon catalysts

ORR catalysts	Precursor	Activation	Onset potential (V vs. RHE)	Half-wave potential (V vs. RHE)	Electrolyte	Ref.
BZ-800	*Bacillus subtilis*	$ZnCl_2$	0.91	0.76	0.1M KOH	[1]
SA-CNF-900	Spider silk	$ZnCl_2$	0.98	0.85	0.1M KOH	[2]
BCZA-9-1/2	Soybean	$ZnCl_2$	0.95	0.84	0.1M KOH	[3]
N-CSs	Fermented rice	$ZnCl_2$	0.85	0.81	0.1M KOH	[4]
WHC-700	Water hyacinth	$ZnCl_2$	0.98	0.85	0.1M KOH	[5]
NCN	Chitosan	Urea	0.94	0.78	0.1M KOH	[6]
HC-900	Human hair	NaOH	0.95	0.80	0.1M KOH	[7]
LC2-700H	London plane	KOH	0.87	0.70	0.1M KOH	[8]
NC	Okara	$FeCl_3$	0.98	0.86	0.1M KOH	[9]
BP350C1000	Blood protein	/	0.90	0.78	0.1M KOH	[10]
FCN	Soy milk	/	0.87	0.79	0.1M KOH	[11]
Fe-CEW	Egg white	$FeCl_3$	0.89	0.80	0.1M KOH	[12]
Fe/N/CNT@PCFs	Catkin	$FeCl_3$	0.92	0.83	0.1M KOH	[13]
CFB	Fish bones	$FeCl_3$	0.96	0.87	0.1M KOH	[14]
$AC900NH_3$	Luffa sponge	KOH	0.97	0.86	0.1M KOH	[15]
N-OMCs-800	Honey	/	0.89	0.79	0.1 M KOH	[16]
SI-AZ-800	Gastrodia elata	$ZnCl_2$	0.96	0.82	0.1 M KOH	[17]
Scup-1000	Seaweed	/	0.96	0.81	0.1 M KOH	[18]
TMC900	Moss	/	0.94	0.83	0.1 M KOH	[19]
HAZ-800	Bamboo fungus	$ZnCl_2$	0.94	0.79	0.1 M KOH	[20]
NPCNs	Ginkgo leaves	NH_3	0.92	0.77	0.1 M KOH	[21]
N-CNAs	Monkey grass	/	0.94	0.81	0.1 M KOH	[22]
CS900-ACs	Silk fibroin	Steam	0.83	/	0.5 M H_2SO_4	[23]
GF-700	Silk	KCl	0.58	0.40	0.5M H_2SO_4	[24]
PAC-800	**Cocoon Silk**	**$ZnCl_2$**	**0.99**	**0.83**	0.1M KOH	**This work**

/ Not mentioned.

The potentials were converted with these equations below:

$E_{RHE}= E_{SCE}+0.2438\ V+0.0591\times pH$

$E_{RHE}= E_{Ag/AgCl}+0.197\ V+0.0591\times pH$

Reference:

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Figure S1

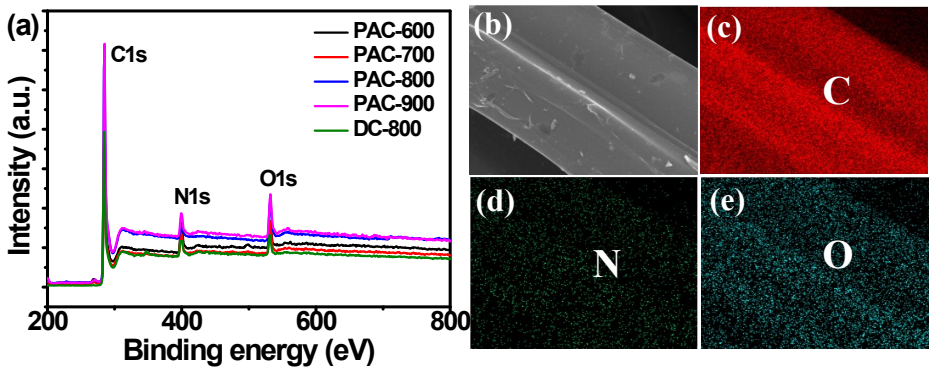

Fig. S1 Survey XPS of PAC-600, PAC -700, PAC-800, PAC -900 and DC-800 (a); SEM image (b) and the corresponding quantitative EDS element mapping of C, N and O of PAC-800 (c ~ e).

Figure S2

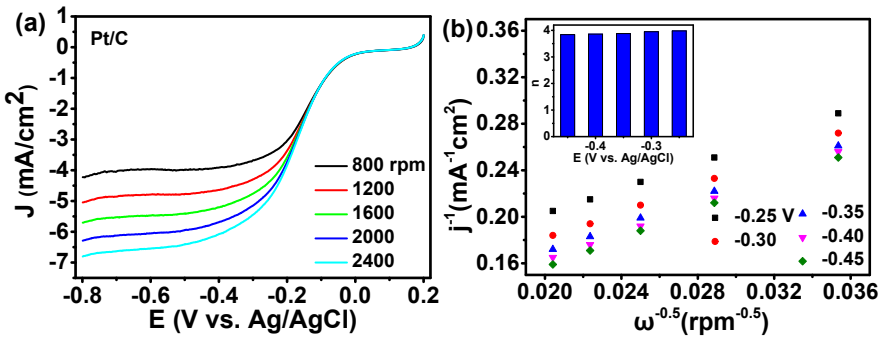

Fig. S2 (a): LSV curves of Pt/C catalyst in O_2-saturated 0.1 M KOH solution at scan rate of 10 mV s^{-1} at different rotation rates from 800 to 2400 rpm, (b): the corresponding K-L plots at different potentials of Pt/C catalyst, and the insert is the electron transfer numbers during the ORR process.