Rationally Constructing Nitrogen-Fluorine Heteroatoms on Porous-carbon Derived from Pomegranate-Fruit Peel-waste Towards Efficient Oxygen Reduction Catalyst for Polymer Electrolyte Membrane Fuel Cells

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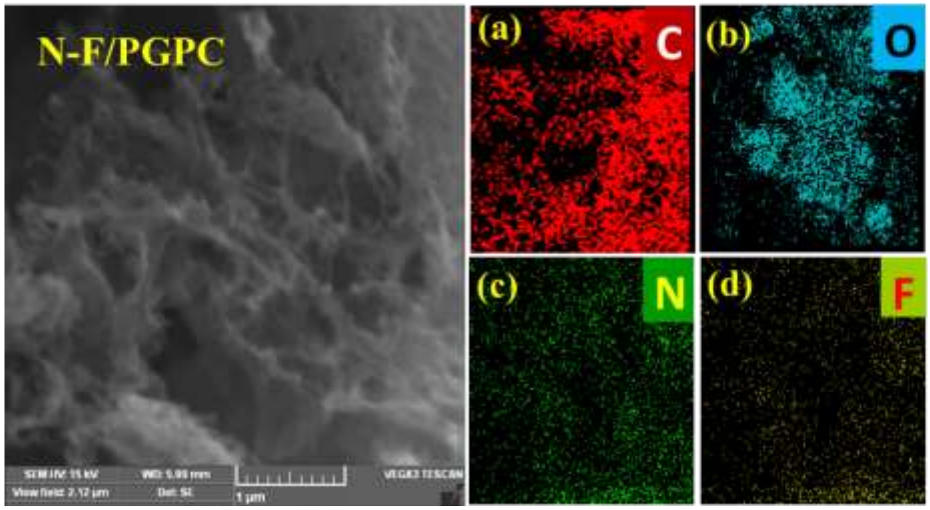

Fig. S1. The FE-SEM elemental mappings of N-F/PGPC catalyst showing the uniform distribution of heteroatoms (C, O, N and F) in the carbon matrix.

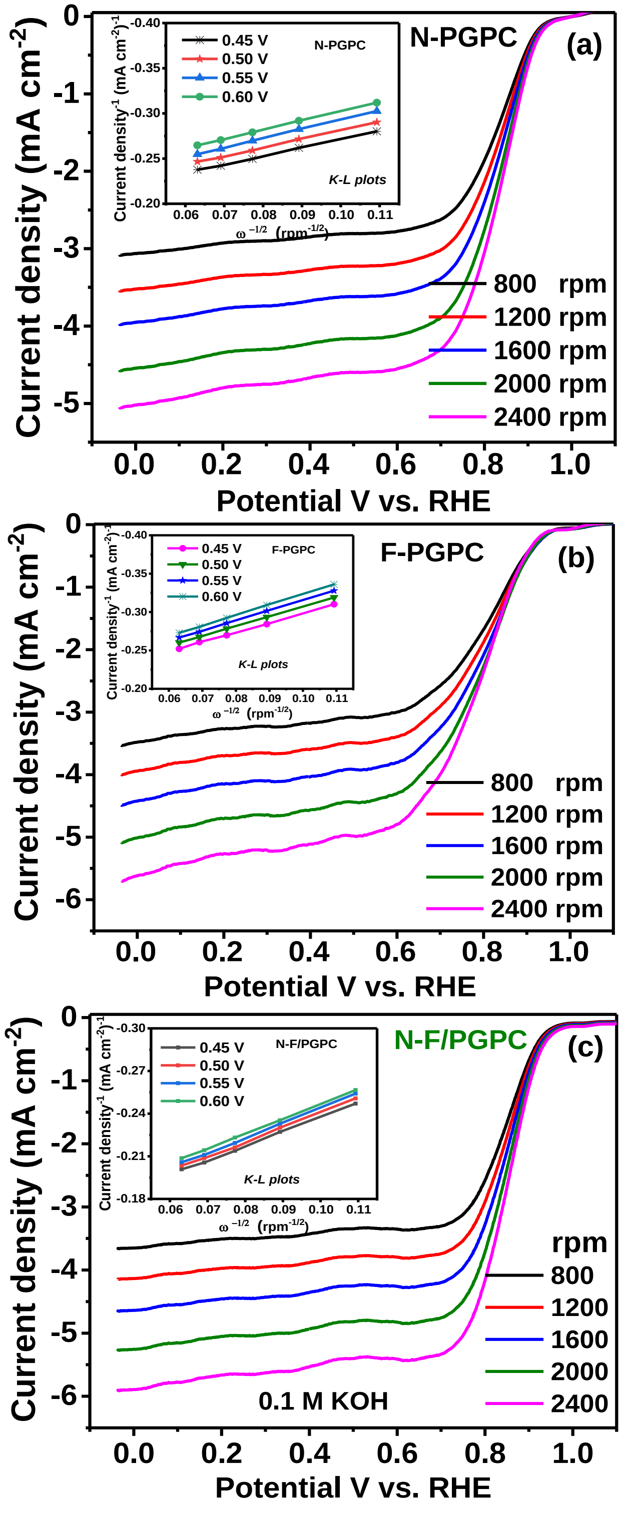

Fig. S2. Hydrodynamic voltammograms of (a) N-PGPC, (b) F-PGPC and (c) N-F/PGPC catalysts measured in O_2-saturaretd 0.1 M KOH at 5 mV s^{-1} scan rate. The corresponding K-L plots are located in insets.

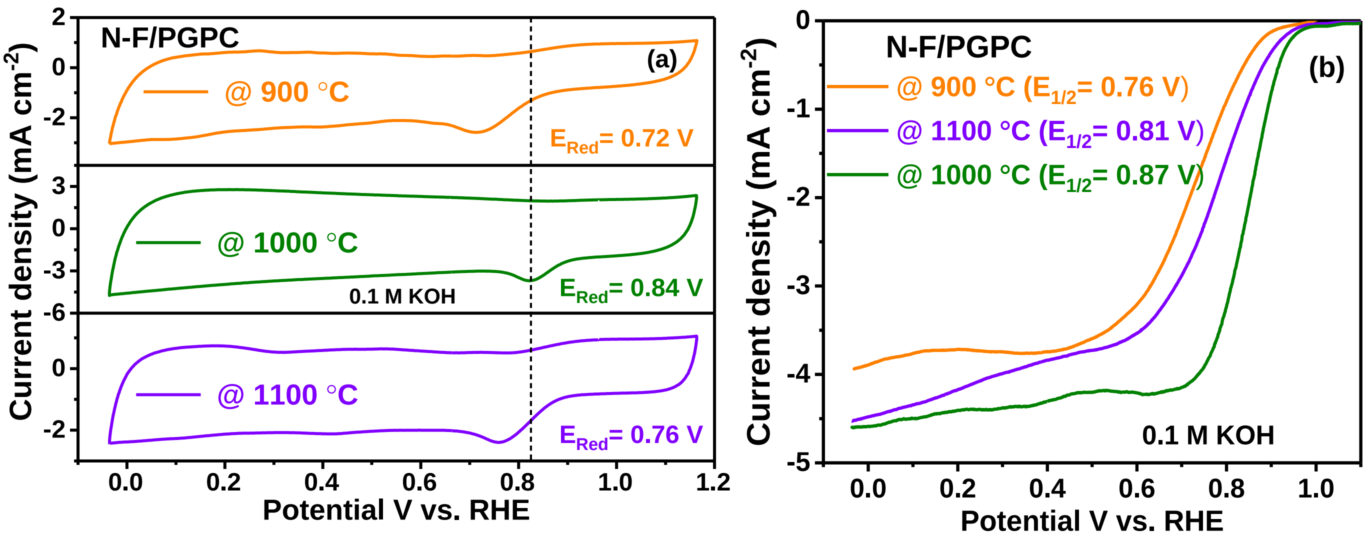

Fig. S3. (a), (b) CVs and LSVs of N-F/PGPC catalyst at different temperatures measured in O_2-saturated 0.1 M KOH aqueous electrolyte, recorded at 50, 5 mV s^{-1} respectively. The corresponding E_{Red}, $E_{1/2}$ potentials are pointed in the figures.

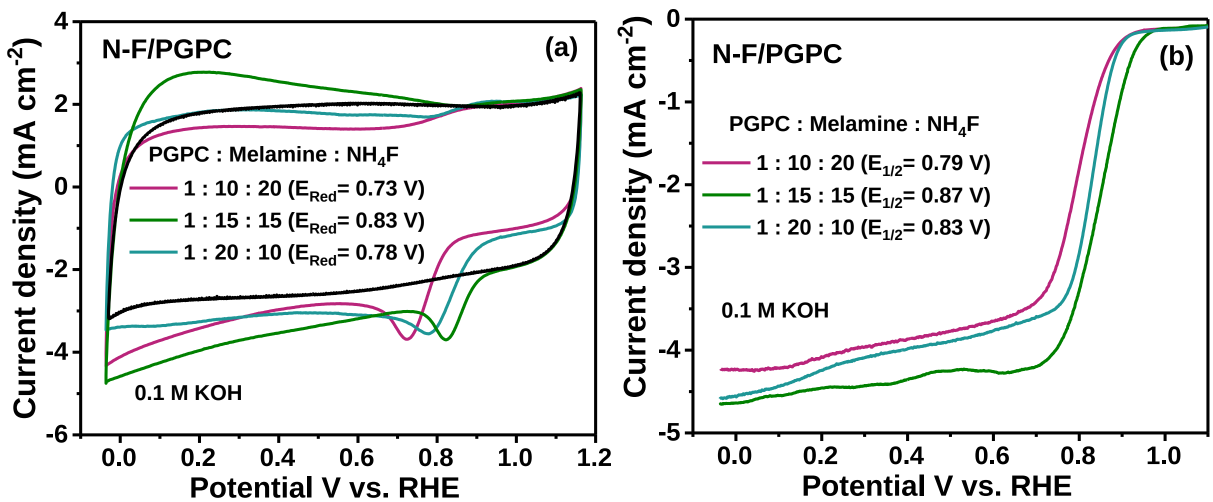

Fig. S4. (a), (b) CVs and LSVs of N-F/PGPC catalyst at different weight ratios of PGPC: melamine: NH_4F measured in O_2-saturated 0.1 M KOH aqueous electrolyte, recorded at 50, 5 mV s^{-1} respectively. The corresponding E_{Red}, $E_{1/2}$ potentials are pointed in the figures.

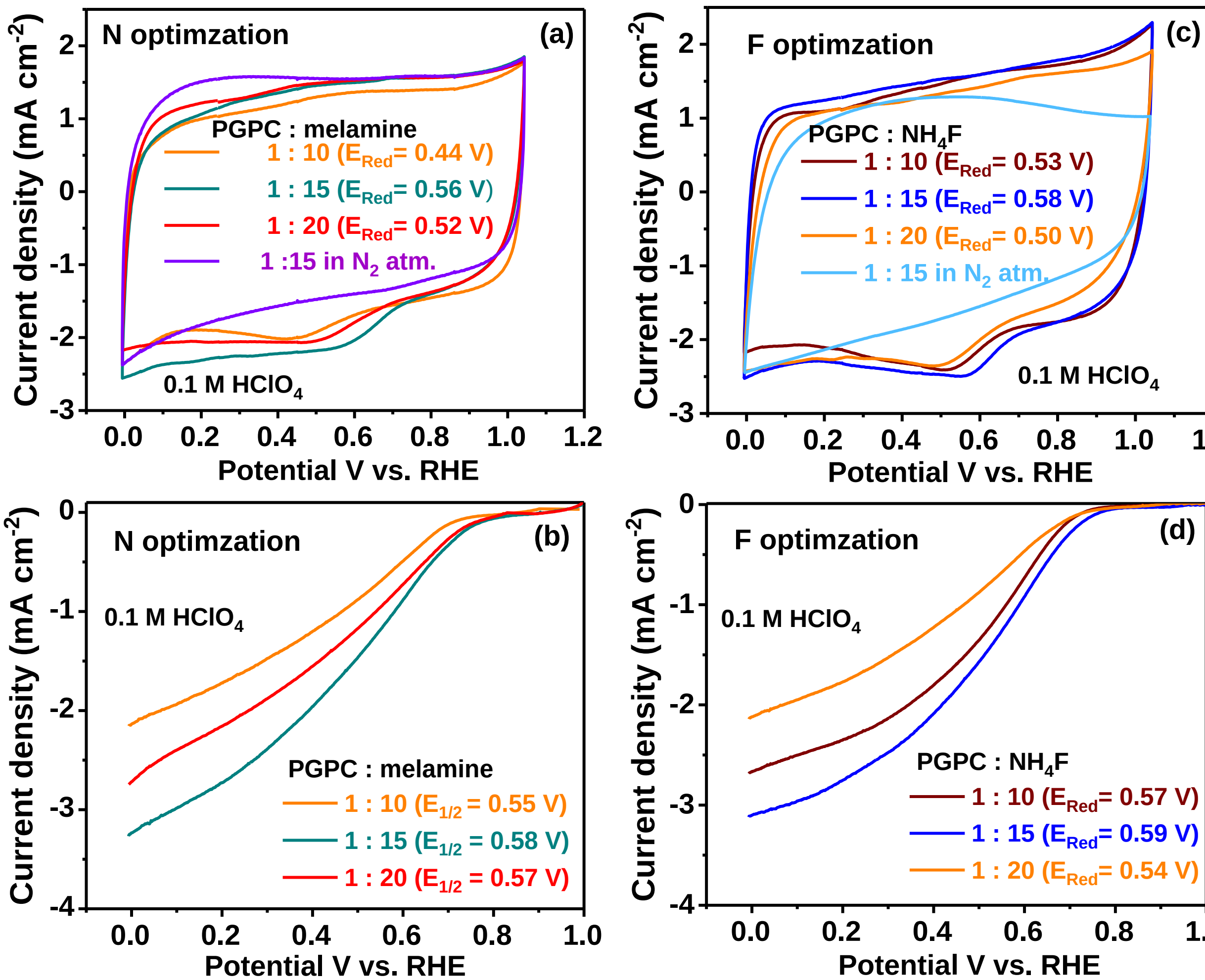

Fig. S5. (a,c) CVs for N, F optimizations at different mass ratios of PGPC to melamine and PGPC to NH_4F respectively at 50 mV s^{-1} scan rate respectively, (b,d) the corresponding LSVs at 5 mV s^{-1} scan rate, recorded at 1600 rpm rotation rate in O_2-saturaretd 0.1 M $HClO_4$. The corresponding E_{Red}, $E_{1/2}$ potentials are reported.

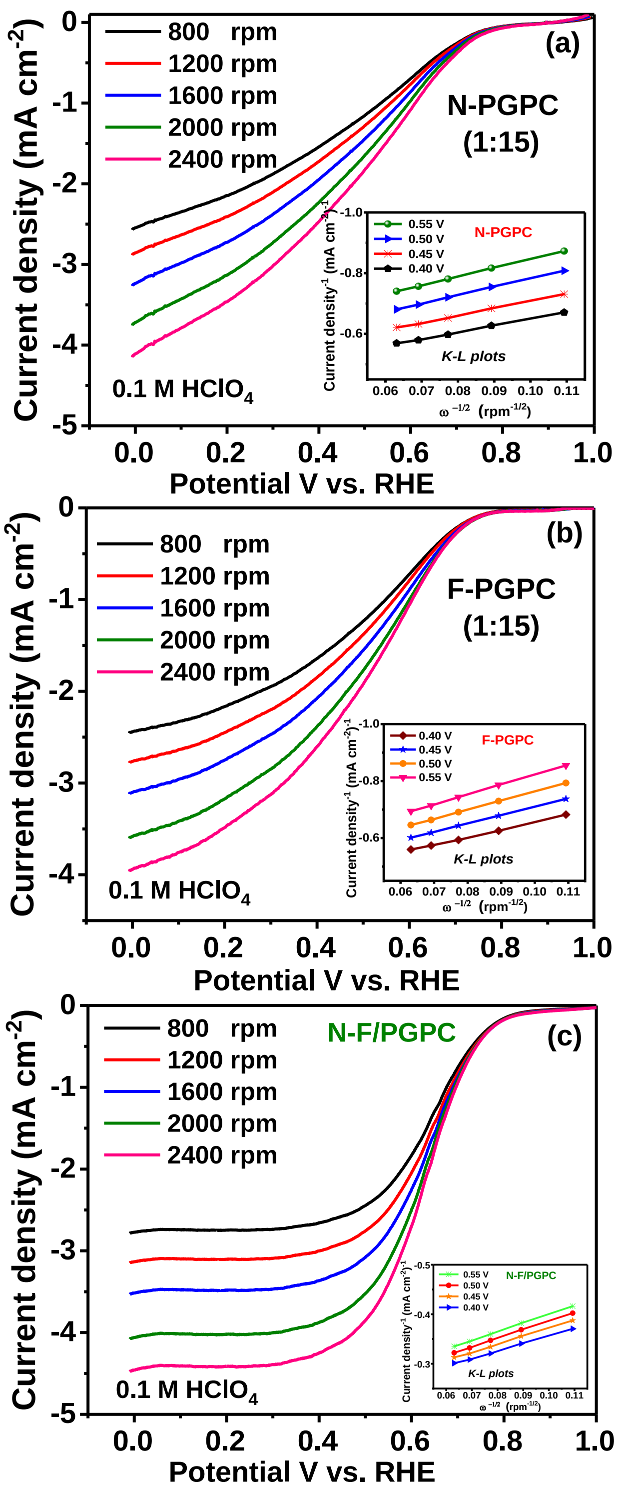

Fig. S6. Hydrodynamic voltammograms of (a) N-PGPC, (b) F-PGPC and (c) N-F/PGPC catalysts measured in O_2-saturaretd 0.1 M $HClO_4$ at 5 mV s^{-1} scan rate. The corresponding K-L plots are pointed in insets.

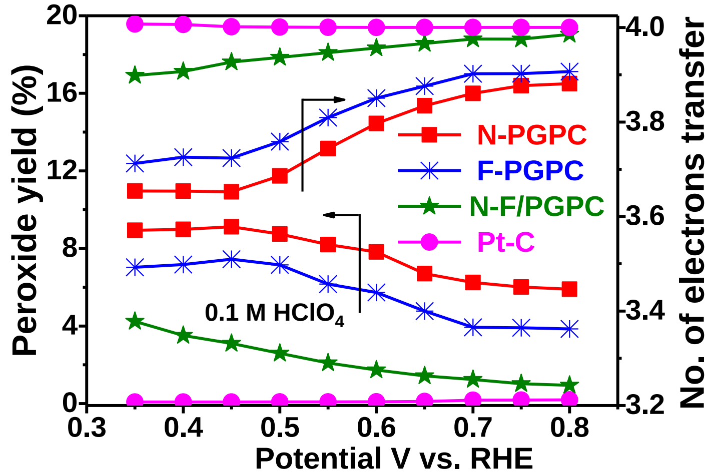

Fig. S7. Number of electron transfer, HO_2^- produced during ORR process in 0.1 M $HClO_4$ electrolyte.

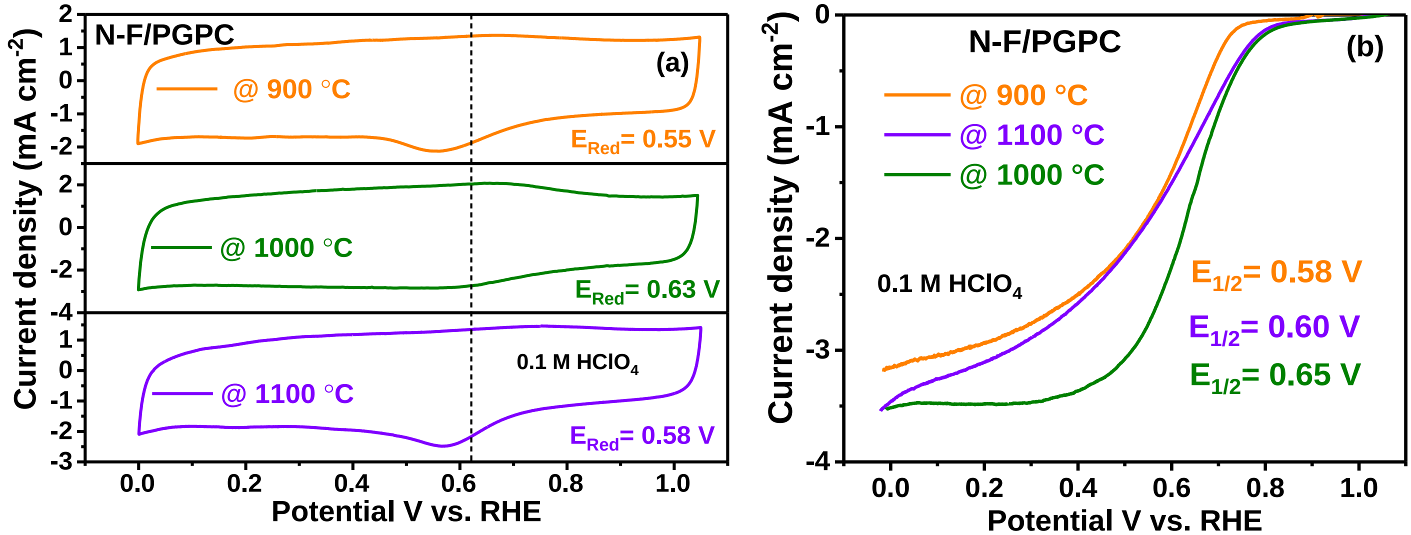

Fig. S8. (a), (b) CVs and LSVs of N-F/PGPC catalyst at different temperatures measured in O_2-saturated 0.1 M $HClO_4$ aqueous electrolyte, recorded at 50, 5 mV s^{-1} respectively. The corresponding E_{Red}, $E_{1/2}$ potentials are pointed in the figures.

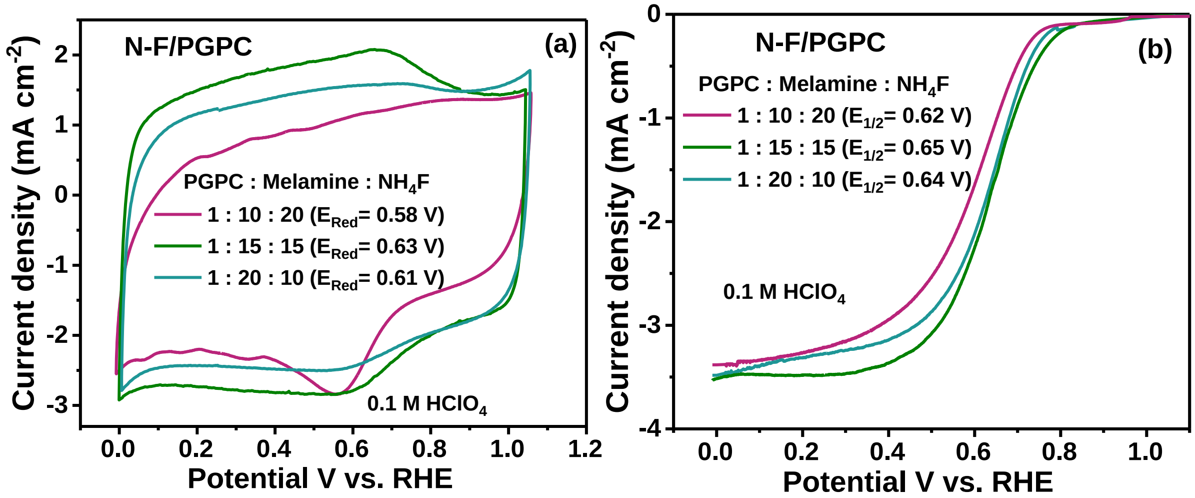

Fig. S9. (a), (b) CVs and LSVs of N-F/PGPC catalyst at different weight ratios of PGPC: melamine: NH_4F measured in O_2-saturated 0.1 M KOH aqueous electrolyte, recorded at 50, 5 mV s^{-1} respectively. The corresponding E_{Red}, $E_{1/2}$ potentials are pointed in the figures.

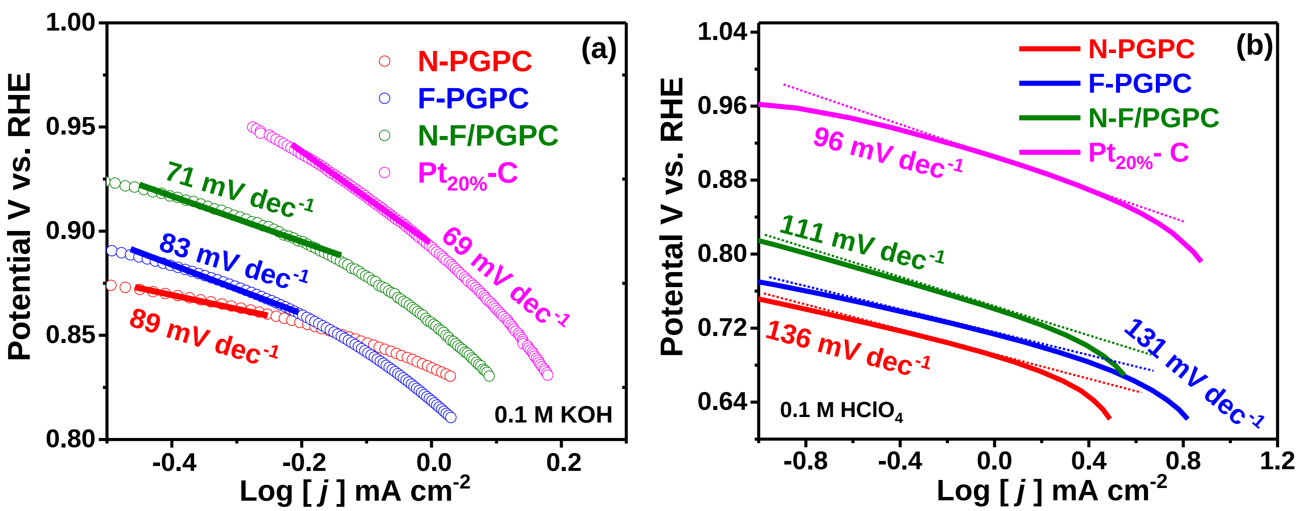

Fig. S10. Tafel plots and the corresponding slope values for N-PGPC, F-PGPC, N-F/PGPC and $Pt_{20\%}$-C catalysts in the higher potential region- (a) O_2-saturated 0.1 M KOH; (b) O_2- saturated 0.1 M $HClO_4$ electrolytes.

Table S1. The performance of various catalysts in alkaline electrolyte (KOH/NaOH) developed from the renewable sources reported in the literature.

S. No.	Source of carbon	Synthetic process & doped elements (pyrolysis temperature / °C)	Specific / BET surface area (m^2 g^{-1})	Catalyst loading mg cm^{-2}	Electrochemical parameters (V vs. RHE)		Ref. [S]
					Onset (V)	$E_{1/2}$ (V)	
1.	Ginkgo Leaves	Pyrolysis @900-1100 & N,P,S	486	0.2	0.91	0.76	1
2.	Silk Cocoon	Pyrolysis @700-900 & N,S	377	0.199	0.85	0.71	2
3.	Pulsatilla Chinensis Regel	Pyrolysis @700-1000 & N,P	---	0.2	---	0.82	3
4.	China Rose	Pyrolysis @ 900 & N,S, O	1478	0.15	0.87	--	4
5.	Sweet Osmanthus Fruit	Pyrolysis @ & N,S, P	431	0.31	0.96	---	5
6.	Chrysanthemum Flowers	Pyrolysis @700-900 & N, S	810	0.12	1.05	---	6
7.	Sophora Flower	Pyrolysis @700-900 & N,S	1815	0.2	0.92	0.72	7
8.	Mulberry Leaves	Pyrolysis @ 700-900 & N,S	1689	0.204	0.86	---	8
9.	Lotus Leaves	Pyrolysis @ 800-1000 & N,S	908	0.658	0.87	0.81	9
10.	Silk Cotton	Pyrolysis @ 1000 & N,F	950	0.5	0.86	0.82	10
11.	Waste Lotus Seedpod	Pyrolysis @ 700-900 & N,P	269	0.1	0.87	---	11
12.	Willow Catkins	Pyrolysis @ 550- 950 & N,P	257	0.204	0.76	---	12
13.	Shaddock Peel	Pyrolysis @ 600-900 & N, P	548	0.283	---	0.83	13
14.	Waste Pomelo Peels	Pyrolysis @ 1000 & N,S	869	0.85	0.85	---	14
15.	Fructus Azedarach	Pyrolysis @ 900 & N,P	1706	0.418	0.94	0.84	15
16.	Eggplant	Pyrolysis @ 900 & K, Cl, O	1051	0.12	0.83	0.71	16
17.	Sweet Potato Vines	Pyrolysis @ 800 & N, S	885	0.1	0.94	0.84	17
18.	Coconut Shells	Pyrolysis @ 1000 & N, P	1216	0.1	0.81	0.78	18
19.	Garlic Stems	Pyrolysis @ 600-1000 & N, P	991	0.247	0.97	0.89	19
20.	Yams	Pyrolysis @ 700-900 & N, S	964	0.12	0.94	0.82	20
21.	Bean Sprout	Pyrolysis @ 900 & N, P	572	0.23	0.93	0.82	21
22.	Cellulose Nano fibrils	Pyrolysis @ 900 & N, S	612	0.25	0.84	---	22
23.	Basswood Block	Pyrolysis @ 950 & N, S	1438	0.28	0.98	0.86	23
24.	Bamboo Stems	Pyrolysis @ 700-900 & N, S	753	1.0	---	0.81	24
25.	Sisal Rejects/Rope Industry	Pyrolysis @ 800 & N, S	1419	0.12	0.84	---	25
26.	Sugarcane Vinasse	Pyrolysis @ 750 & N, S	734	0.1	0.86	0.78	26
27.	Pomegranate Fruit Peels	Pyrolysis @ 900-1100 & N, F	974	0.5	0.92	0.87	**This work**

Table S2. The performance of various catalysts in acidic electrolytes ($HClO_4$/H_2SO_4) developed from the renewable sources reported in the literature.

S. No.	Source of carbon	Synthetic process & doped elements (pyrolysis temperature / °C)	Specific / BET surface area ($m^2 g^{-1}$)	Catalyst loading mg cm^{-2}	Electrochemical parameters (V vs. RHE)		Ref. [S]
					Onset (V)	$E_{1/2}$ (V)	
1.	Multiwall carbon nanotubes	Pyrolysis @ 1000 & N, F	321	1.0	0.64	0.55	27
2.	SO_3H-PANI/Ketjenblack	Pyrolysis @ 1000 & N, S, F	1000	1.0	0.71	0.63	28
3.	Spent coffee grounds	Pyrolysis @ 1000 & N,F	975	0.5	0.79	0.73	29
4.	Sweet osmanthus fruit	Pyrolysis @ & N,S, P	431	0.31	0.44	0.32	30
5.	Graphene	Pyrolysis @ 900 & B, N, P	800	0.691	0.87	0.64	31
6.	Bombyxmori silk fibroin	Pyrolysis @ 700-1500 & N,O	1018	0.2	0.79	0.62	32
7.	Waste leather	Pyrolysis @ 900 & N, S, Fe	746	0.3	0.82	0.74	33
8.	Sheep horn	Pyrolysis @ 600-900 & N,S	313	0.4	0.81	0.72	34
9.	Sewage sludge	Pyrolysis @ 800 & N, S	265	0.1	0.57	0.51	35
10.	Seaweed	Pyrolysis @ 900 & N, O	1377	0.4	---	0.60	36
11.	Carbon nanotubes	Pyrolysis @ 900 & N, S	149	0.2	0.52	0.42	37
12.	Keratin	Pyrolysis @ 1000 & N, S	953	0.408	0.45	0.34	38
13.	Graphite nanofibers	Pyrolysis @ 1000 & N, F	----	1.0	0.78	0.63	39
14.	Carbon nanofibers	Pyrolysis @ 1000 & N, F	709	0.3	0.94	0.81	40
15.	China rose	Pyrolysis @ 900 & N, S, O	1478	0.15	0.59	0.44	41
16.	Chitosan	Pyrolysis @ 600 & N, B	796	0.383	0.79	0.58	42
17.	Cysteine	Pyrolysis @ 800 & N, S	1309	0.408	0.81	0.61	43
18.	Feculae bombycis	Pyrolysis @ 800 & N, S, P	435	0.3	0.64	0.57	44
19.	Fructus azedarach	Pyrolysis @ 900 & N, P	1706	0.418	0.91	0.80	45
20.	Allium cepa	Pyrolysis @ 900 & N, S	1859	0.141	0.63	----	46
21.	Porous graphene foams	Pyrolysis @ 900 & B, N, P	670	0.2	0.85	0.68	47
22.	Phytic acid super-molecular aggregate	Pyrolysis @ 1000 & N, P, Co	952	0.31	0.91	0.79	48
23.	Porous carbon-CNTs	Pyrolysis @ 800 & N, P, Co	---	0.24	0.92	0.81	49
24.	Graphitic carbon spheres	Pyrolysis @ 1000 & N, S, Fe	371	0.4	0.85	0.73	50
25.	Carbon nanotubes	Pyrolysis @ 900 & N, O, S	149	0.2	0.44	0.28	51
26.	Dicyandiamide	Pyrolysis @ 900 & N, P	578	0.245	0.6	----	52
27.	Pomegranate fruit peels	Pyrolysis @ 900-1100 & N, F	974	0.5	0.77	0.65	**This work**

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