SUPPORTING INFORMATION

Insights into the electrocatalytic activity of Fe,N-glucose/carbon nanotube hybrids for the oxygen reduction reaction

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Abstract: Glucose-derived carbon hybrids were synthesized by hydrothermal treatment in the presence of oxidized carbon nanotubes. Additionally, iron and nitrogen functionalities were incorporated into the carbon structure using different methodologies. The introduction of iron and nitrogen in a single step under a H_2 atmosphere favored the formation of quaternary nitrogen and oxidized nitrogen, whereas the incorporation of nitrogen under an N_2 atmosphere after doping the hybrids with iron mainly produced pyridinic nitrogen. The samples were characterized by scanning electron microscopy, X-ray spectroscopy, adsorption isotherms, inductively coupled plasma optical emission spectrometry, and Raman spectroscopy. The presence of iron and nitrogen in the carbons increases the onset potential toward oxygen reduction in KOH 0.1 mol L^{-1} by 130 mV (0.83 V), in comparison to carbonized glucose, whereas the reaction mechanism shifts closer to a direct pathway and the formation of HO_2^- decreases to 25% (3.5 electrons). The reaction rate also increased in comparison to the carbonized glucose, as observed by the decrease in the Tafel slope value from 117 to 61 mV dec^{-1}. Furthermore, the incorporation of iron and nitrogen in a single step enhanced the short-term performance of the prepared electrocatalysts, which may also be due to the higher relative amount of quaternary nitrogen.

Keywords: Carbon-based electrocatalyst; Carbon Nanotubes; Oxygen Reduction Reaction; Nitrogen-doping; Iron.

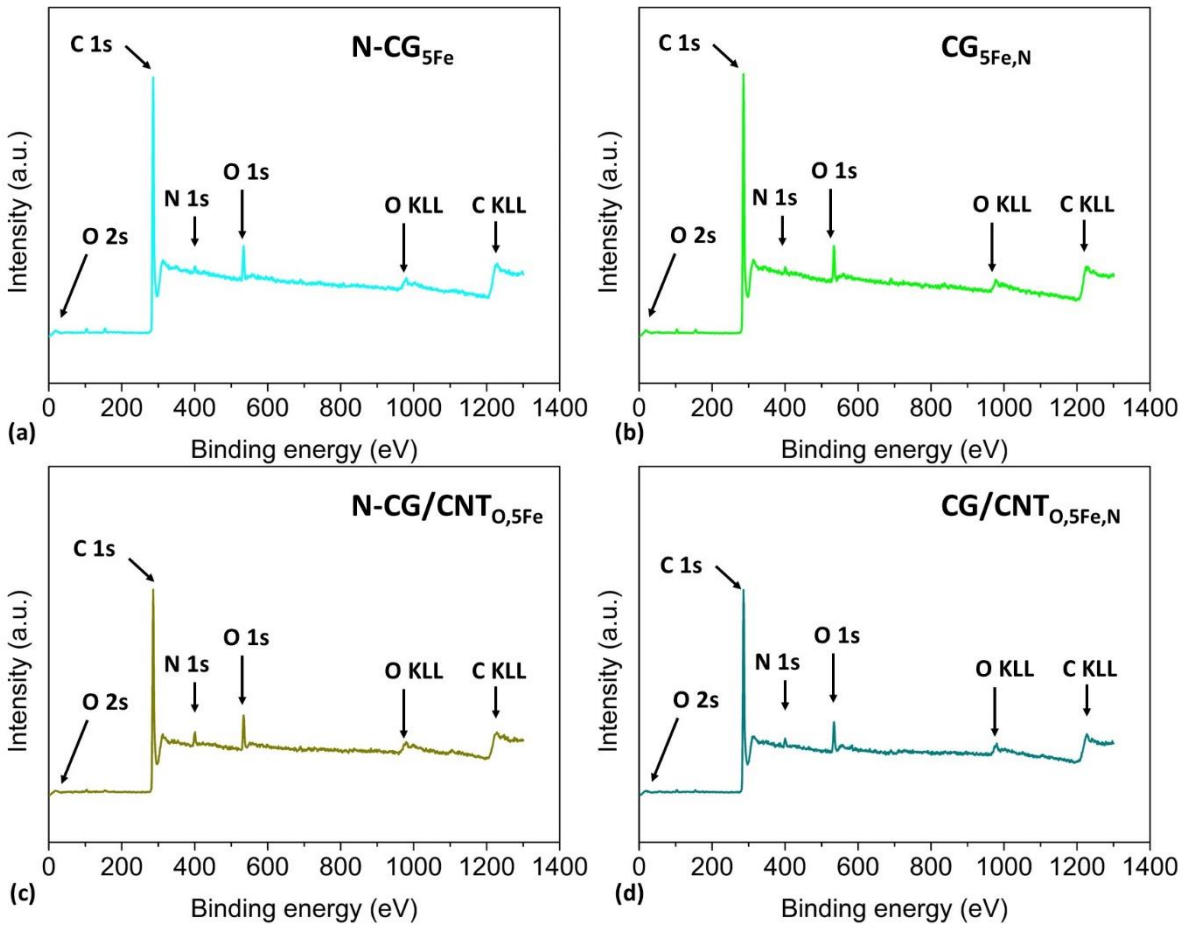

Figure S1. XPS survey spectra of the prepared Fe,N CG (a,b) and Fe,N CG/CNT hybrids (c,d) electrocatalysts, in which N-CG$_{5Fe}$ and N-CG/CNT$_{O,5Fe}$ were prepared using a two-step method and CG$_{5Fe,N}$ and CG/CNT$_O$ were prepared using a one-step method.

Table S1. Surface chemical composition determined by XPS.

Sample	C (wt.%)	O (wt.%)	N (wt.%)
N-CG$_{5Fe}$	91.0	6.2	2.8
N-CG/CNT$_{O,\ 5Fe}$	87.5	7.8	4.7
CG$_{5Fe,N}$	91.4	6.6	2.0
CG/CNT$_{O,5Fe,N}$	89.8	7.5	2.7

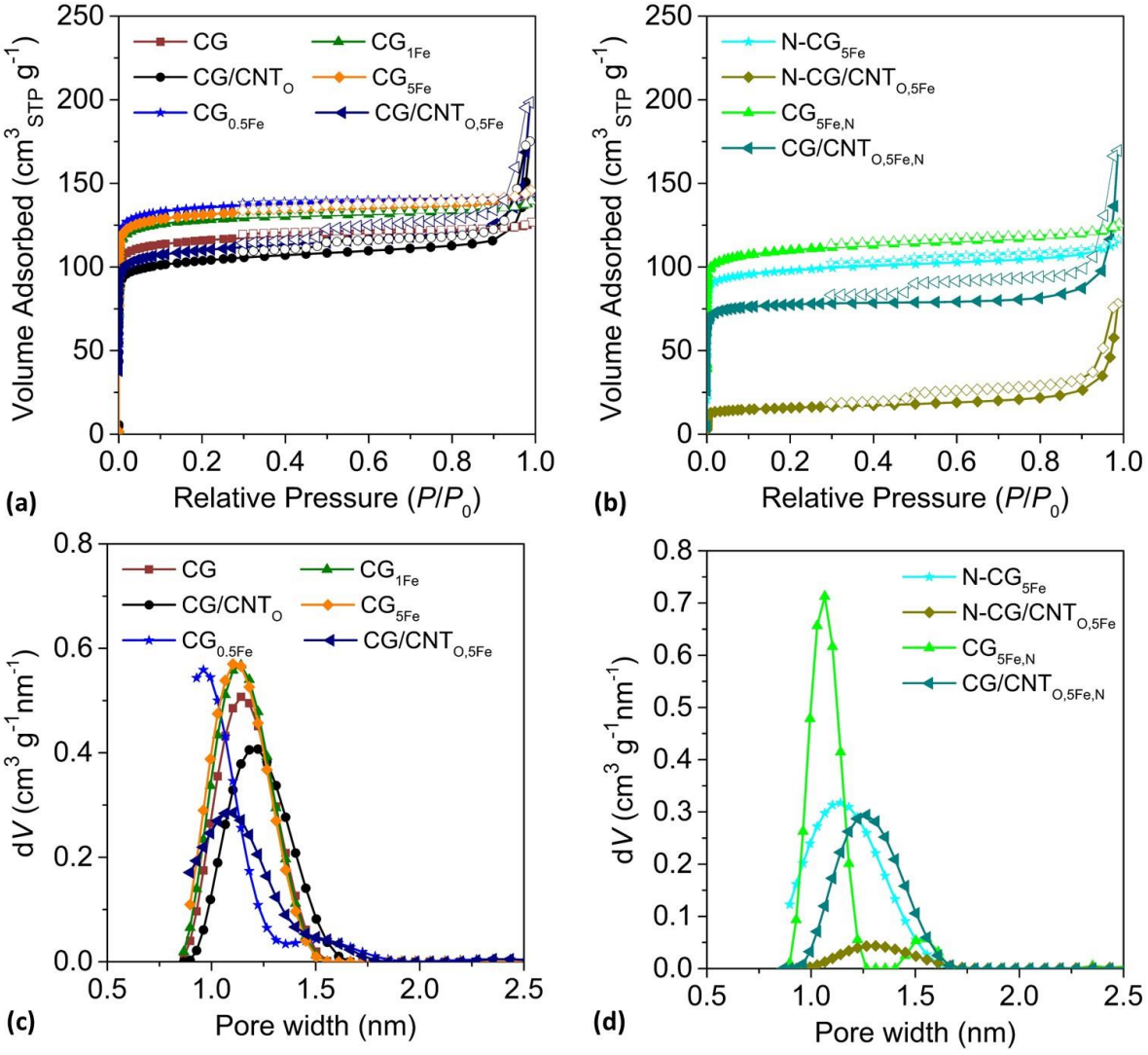

Figure S2. N_2 adsorption-desorption isotherms at -196 °C and pore size distribution of undoped, CG_{XFe} and $CG/CNT_{O,5Fe}$ (a,c), and N-CG_{5Fe}, N-$CG/CNT_{O,5Fe}$, $CG_{5Fe,N}$ and $CG/CNT_{O,5Fe,N}$ (b,d) electrocatalysts.

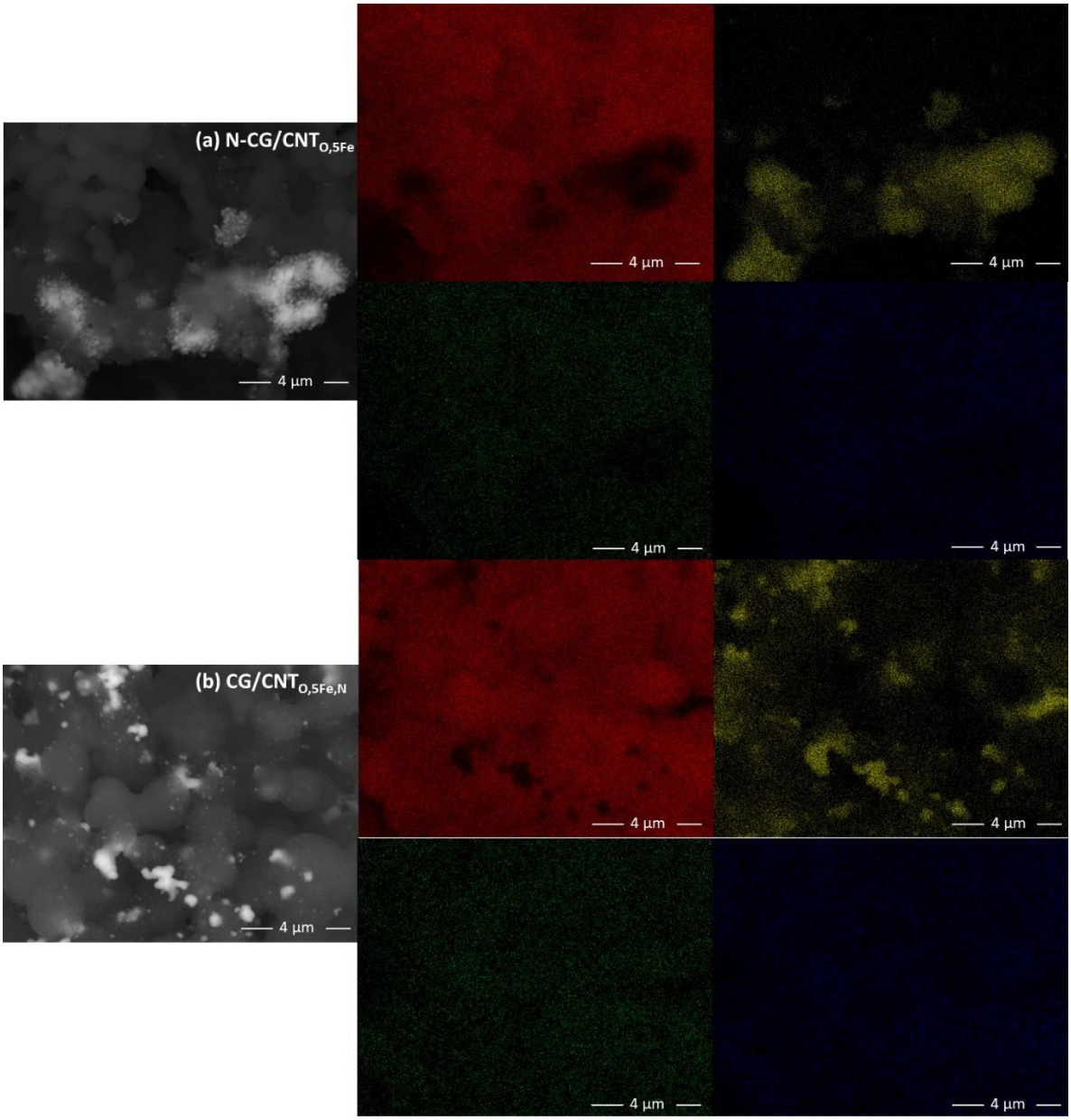

Figure S3. Elemental mapping of N-CG/CNT$_{O,5Fe}$ (a) and CG/CNT$_{O,5Fe,N}$ (b). Red – Carbon, Yellow – Iron, Green – Nitrogen, Blue - Oxygen.

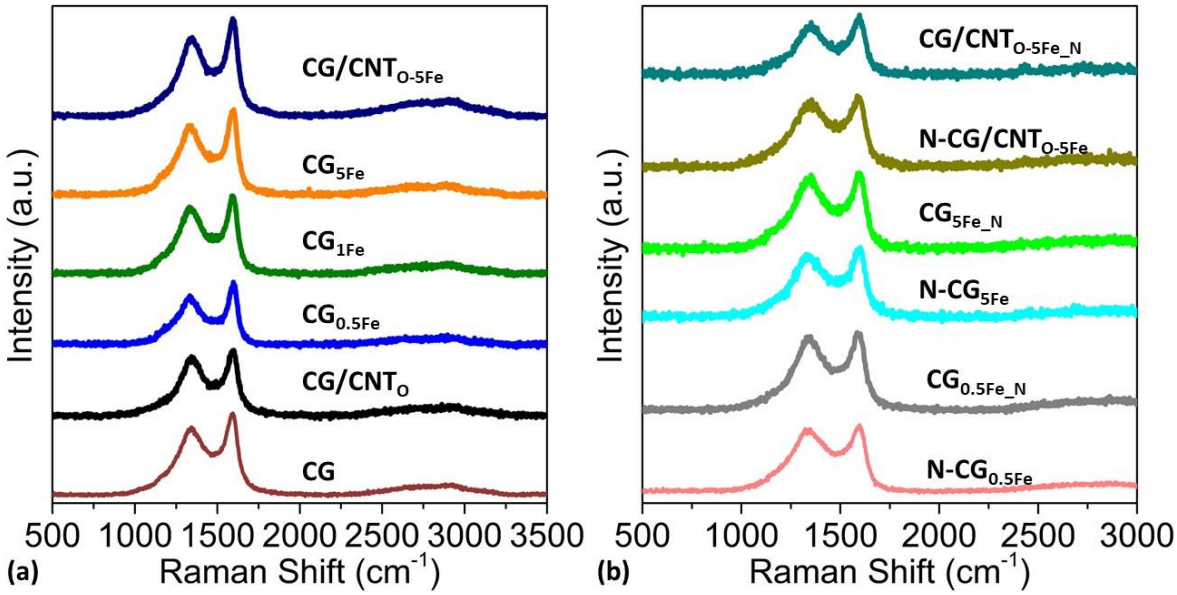

Figure S4. Raman spectra of undoped and monometallic electrocatalysts (a), and Fe,N electrocatalysts (b).

Table S2. Ratio of the integrated D and G peaks obtained by Raman spectroscopy.

Sample	A_D/A_G
CG	2.44
CG/CNT$_O$	2.22
CG$_{0.5Fe}$	2.48
CG$_{1Fe}$	2.44
CG$_{5Fe}$	2.41
CG/CNT$_{O,5Fe}$	2.57
N-CG$_{5Fe}$	2.36
N-CG/CNT$_{O,5Fe}$	2.66
CG$_{5Fe,N}$	2.93
CG/CNT$_{O,5Fe,N}$	2.35

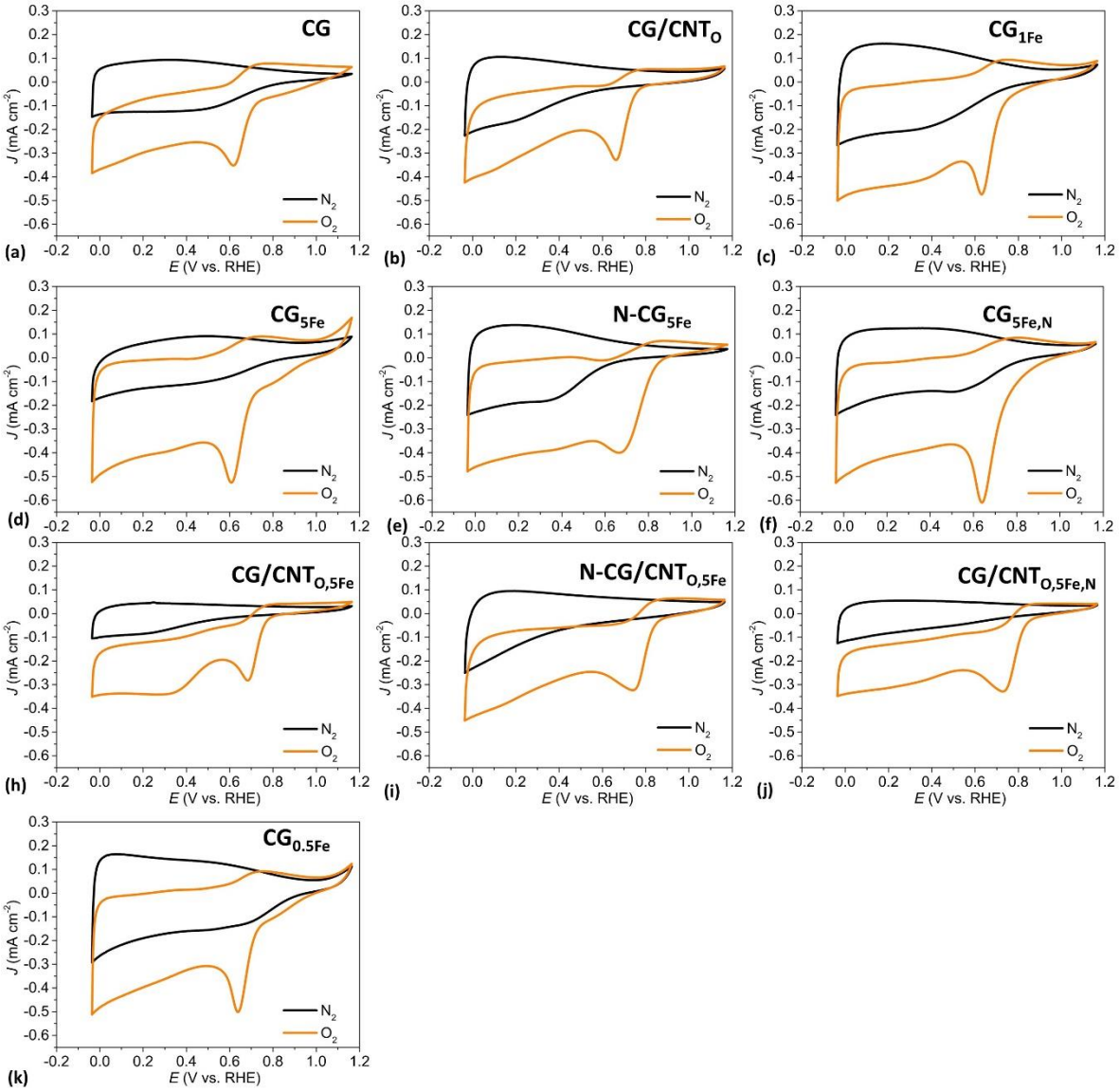

Figure S5. Cyclic voltammograms recorded at 5 mV s^{-1} in N_2- and O_2-saturated 0.1 mol L^{-1} KOH electrolyte from 1.15 V to -0.05 V.

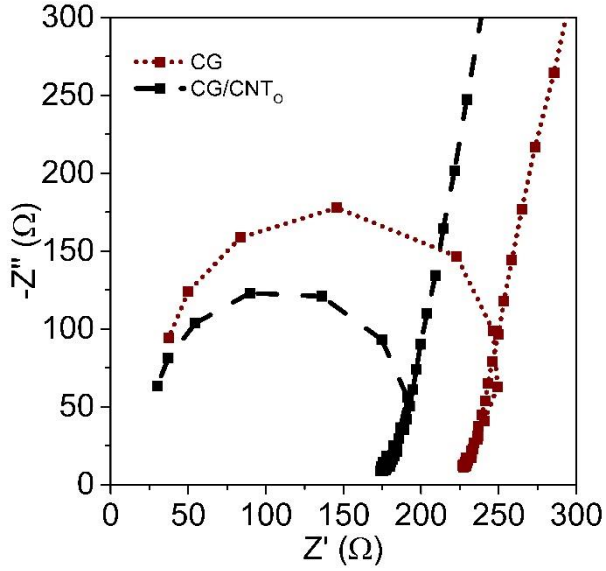

Figure S6. Nyquist plots for CG and CG/CNTO obtained by electrochemical impedance spectroscopy at 0 V.

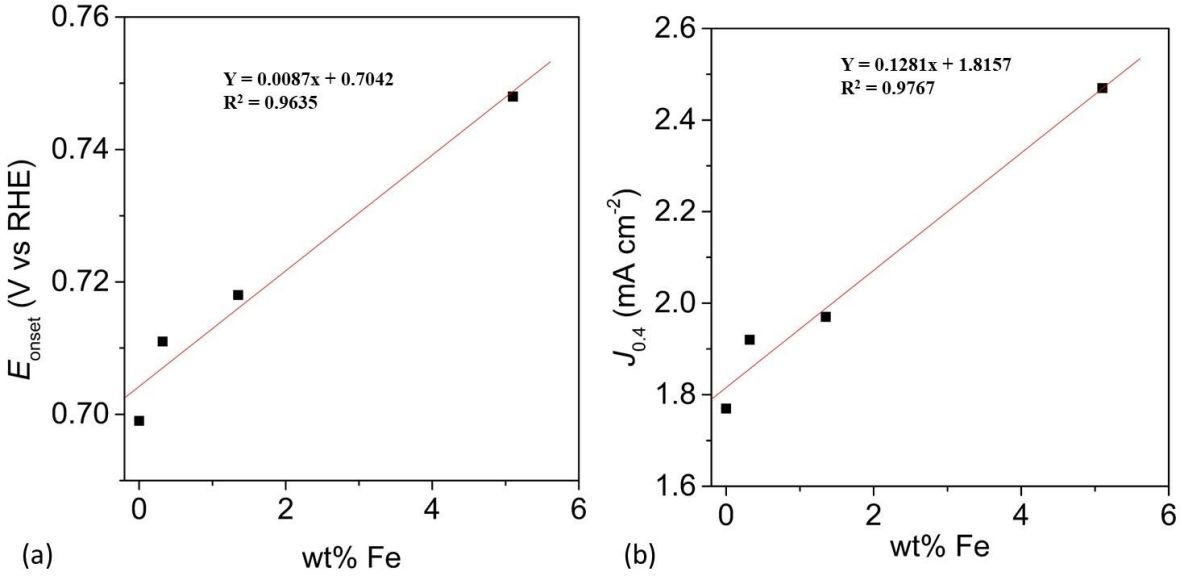

Figure S7. Onset potential (a) and current density at a potential of 0.4 V (b) obtained from the linear sweep voltammetry curves of Fig. 5a (a) for the CGXFe samples versus the percentage of Fe calculated by ICP.

Table S3. ORR parameters of glucose-derived carbons, reagents and synthesis methods employed.

Reagents/Samples	Synthesis Methods	E_{onset} (V)	J_L (mA cm^{-2}) [a]	n_e [a]	*Tafel Slope* (*mV dec^{-1}*)	*Ref.*
N-CG$_{5Fe}$	Hydrothermal Polymerization/ Thermal treatment	0.81	3.4	3.3	52	This work
N-CG/CNT$_{O, 5Fe}$		0.83	3.6	3.3	63	
CG$_{5Fe, N}$		0.79	3.7	3.5	62	
CG/CNT$_{O, 5Fe, N}$		0.81	3.9	3.5	61	
Glucose + dicyandiamide	Activation with $ZnCl_2$	0.92	3.0	3.5-3.9	50-58	[1]
Glucose, melamine, cyanuric acid, dimethyl sulphoxide	Thermal treatment	0.90	4.1	2.5-3.5	-	[2]
Glucose, SBA-15, pluoronic P123, HCl, tetraethyl orthosilicate, H_2SO_4, HF, Thiophene, $FeCl_3$, NH3	Thermal treatment	0.92	5.5	4.0	68	[3]
Glucose, urea, CNT	Thermal treatment	0.95	4.7	3.9	79	[4]
Glucose, thiourea, NaOH, HCl, iron nitrate, urea, sulfur	Thermal treatment, leaching	0.97	5.5	4.0	50-53	[5]
Glucose, dicyandiamide	Thermal treatment	0.95	5.7	3.9	-	[6]
Glucose, Cu_2O, melamine, SiO_2, HNO_3	Thermal treatment	0.89	4.9	4.0	-	[7]
Glucose, $Fe(ClO_4)_2 \cdot xH_2O$, ascorbic acid, NH4COOH, HCOOH, melamine, HCl, methanol	Stirring, thermal treatment	0.92	5.0	3.6	57	[8]
Glucose, urea, $Mg_5(OH)_2(CO_3)_4$, $ZnCl_2$, HCl	Thermal treatment	0.94	5.7	3.2-4.0	52	[9]
Glucose, zinc nitrate, benzimidazole, DMF	Thermal treatment	0.74-0.86	2.5-4.6	2.3-3.7	-	[10]
Glucose, $C_{24}H_{20}P(Br)$, $CH_3(CH_2)_{11}OSO_3Na$,	Hydrothermal treatment/ Carbonization	0.73-0.88	4.0-5.6	3.0-3.8	-	[11]

[a]- Measured at the last LSV point

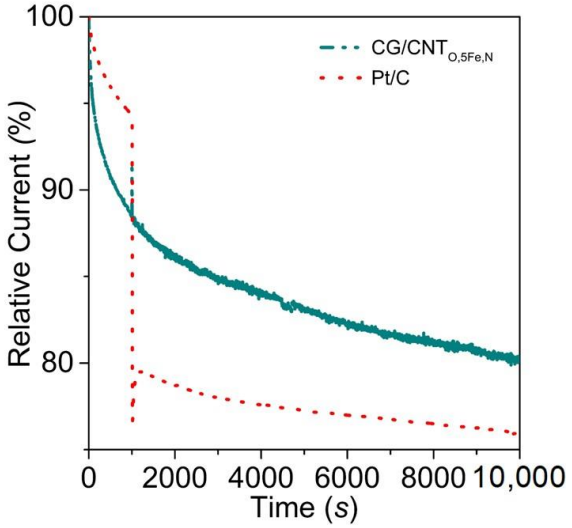

Figure S8. Methanol tolerance of CG/CNT$_{O,5Fe,N}$ and Pt/C at 0.4 V during 10,000 s.

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