

## Heteroatom-Doped Carbon Electrocatalysts Prepared from Marine Biomass Cellulose Nanocrystals and Bio-inspired Polydopamine for Oxygen Reduction Reaction

*Manjit Singh Grewal<sup>1\*</sup>, Yasutaka Matsuo<sup>2</sup> and Hiroshi Yabu<sup>1,3\*</sup>*

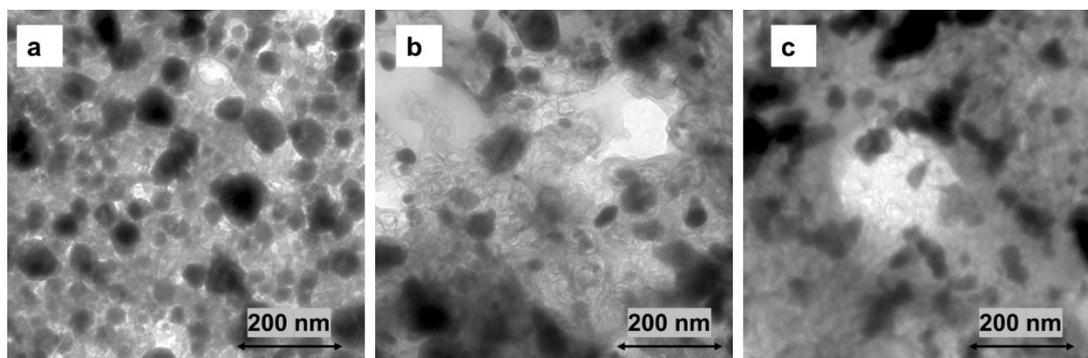
<sup>1</sup>WPI-Advanced Institute of Materials Research (WPI-AIMR), Tohoku University, 2-1-1, Katahira, Aoba-Ku, Sendai 980-8577, Japan.

<sup>2</sup>Research Institute for Electronic Science (RIES), Hokkaido University, N21W10, Kita-Ku, Sapporo, 001-0021, Japan.

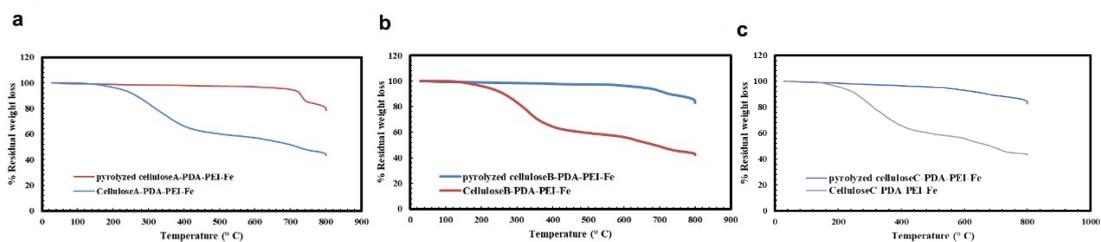
<sup>3</sup>Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, 2-1-1, Katahira, Aoba-Ku, Sendai 980-8577, Japan.

E-mails: [grewal.manjit.singh.d3@tohoku.ac.jp](mailto:grewal.manjit.singh.d3@tohoku.ac.jp), [hiroshi.yabu.d5@tohoku.ac.jp](mailto:hiroshi.yabu.d5@tohoku.ac.jp)

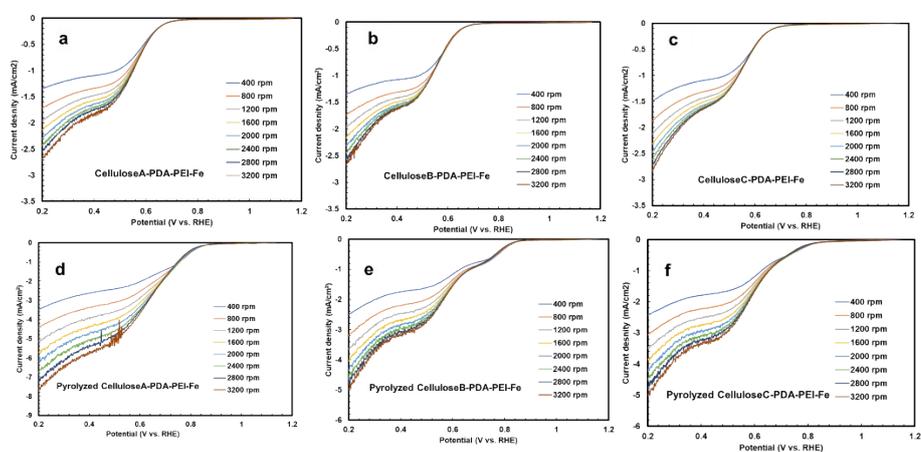
### Supplementary information



**Figure S1:** TEM images (cross-section) of pyrolyzed celluloseA-PDA-PEI-Fe (a), pyrolyzed celluloseB-PDA-PEI-Fe (b), and pyrolyzed celluloseC-PDA-PEI-Fe (c) respectively.



**Figure S2:** TG-DTA curves of (a) CelluloseA-PDA-PEI-Fe and pyrolyzed celluloseA-PDA-PEI-Fe, (b) CelluloseB-PDA-PEI-Fe and pyrolyzed celluloseB-PDA-PEI-Fe, and (c) CelluloseC-PDA-PEI-Fe and pyrolyzed celluloseC-PDA-PEI-Fe respectively.



**Figure S3:** LSV curves of celluloseA-PDA-PEI-Fe (a), celluloseB-PDA-PEI-Fe (b), celluloseC-PDA-PEI-Fe (c), pyrolyzed celluloseA-PDA-PEI-Fe (d), pyrolyzed celluloseB-PDA-PEI-Fe (e), and pyrolyzed celluloseC-PDA-PEI-Fe (f) respectively at 400 rpm to 3200 rpm in  $O_2$ -saturated 0.1 M KOH.

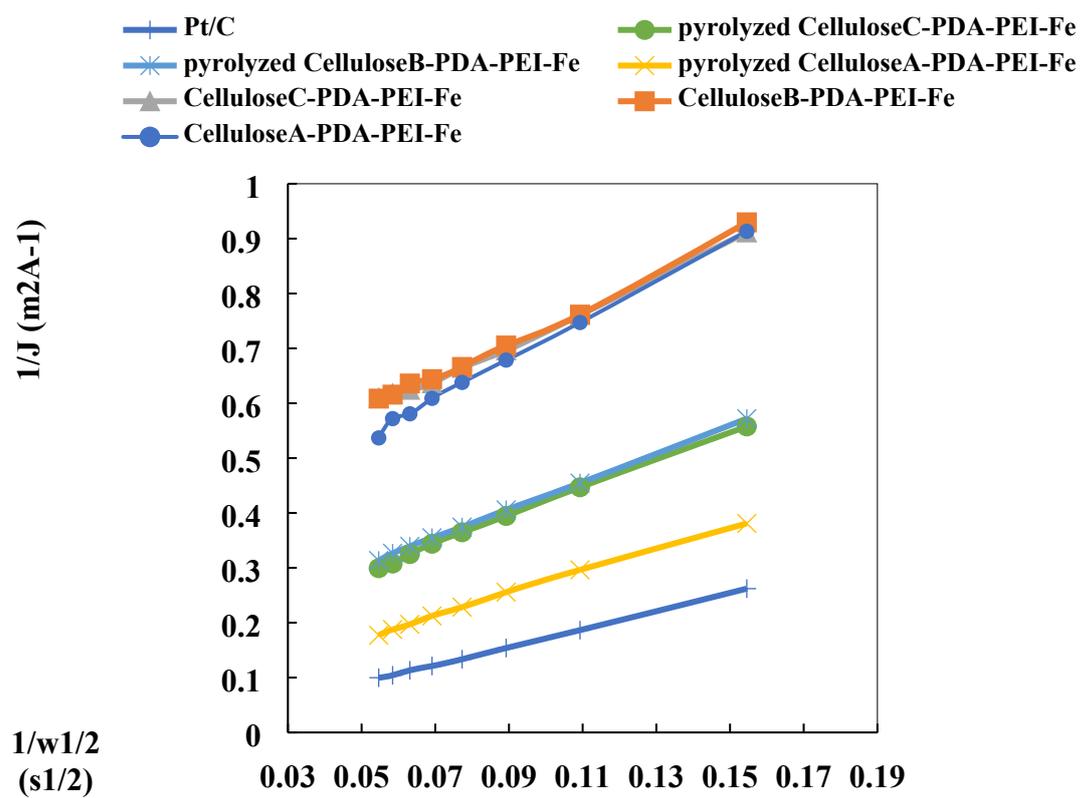
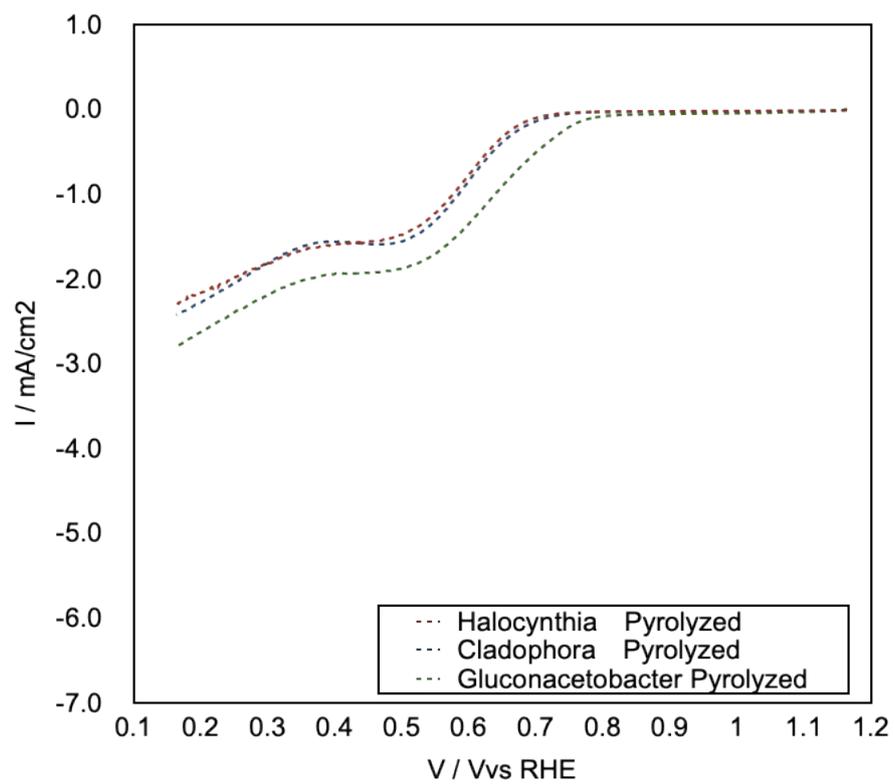
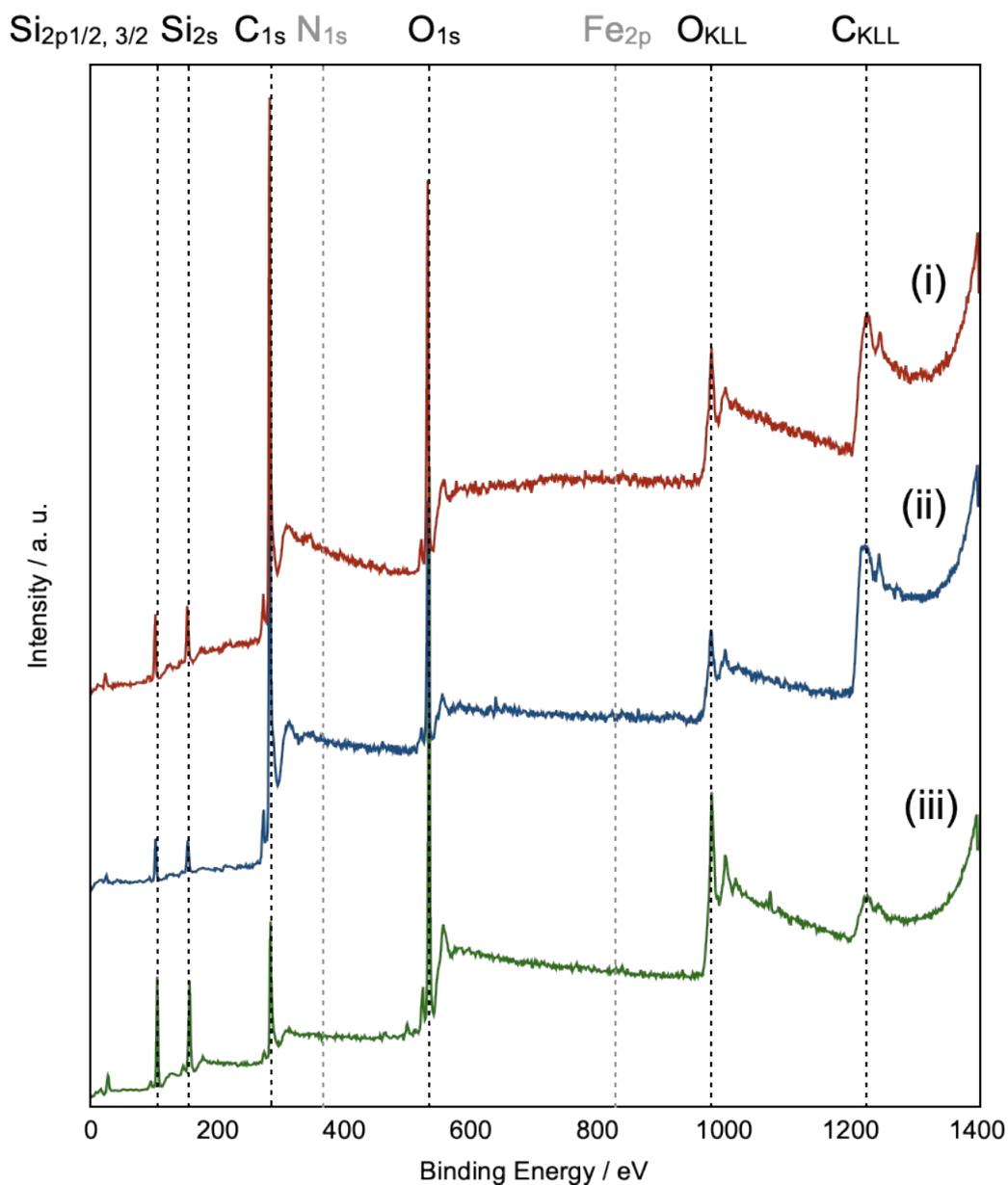


Figure S4: K-L plots derived from S1 plots.

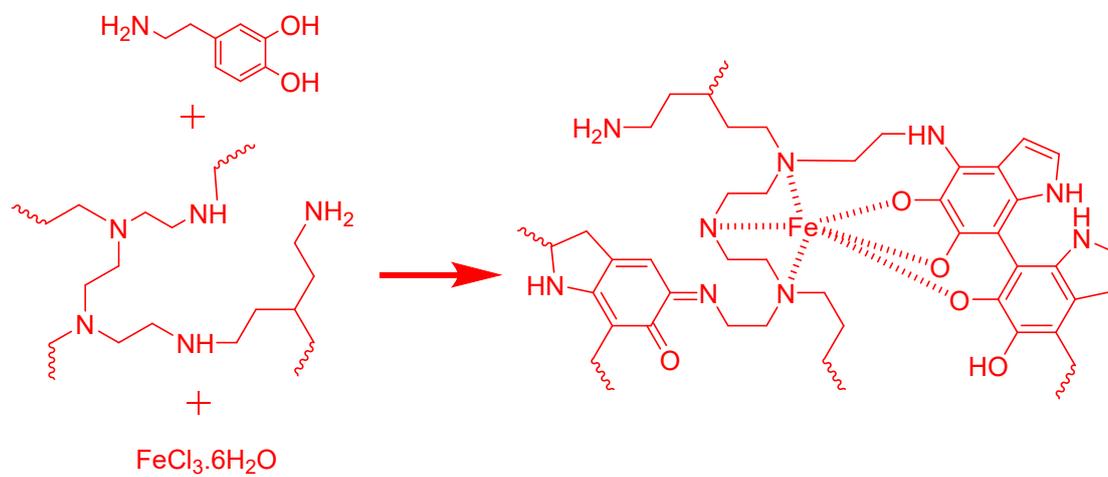


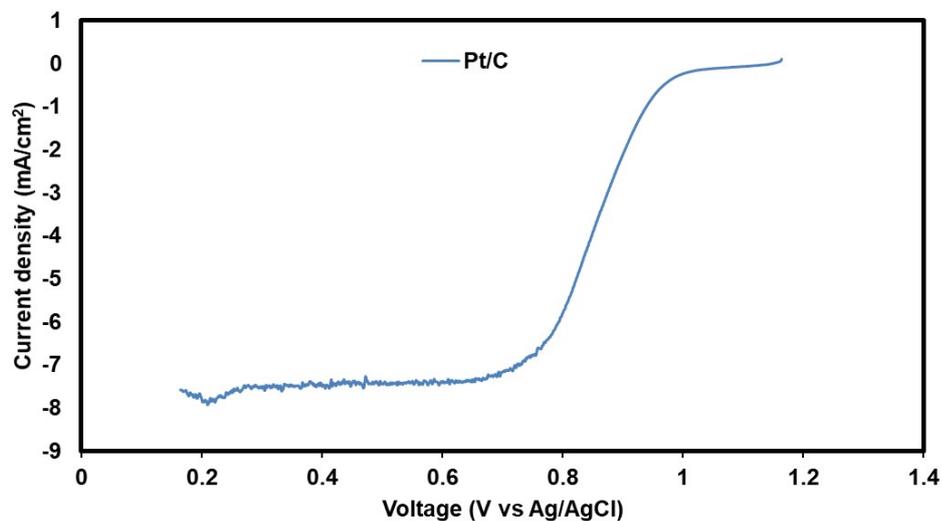
**Figure S5:** LSV curves of pyrolyzed CNCs at 1,600 rpm in O<sub>2</sub>-saturated 0.1 M KOH.



**Figure S6.** Wide scan XPS spectra of pyrolyzed CNCs obtained from *Halocynthia* (i), *Cladophora* (ii) and *Gluconacetobacter* (iii), respectively. No peak attributed to N and Fe was found and there are clear peaks attributed to carbon and Si, O peaks from the substrate.

**Scheme S1:** Reaction scheme for PDA-PEI-Fe coating.

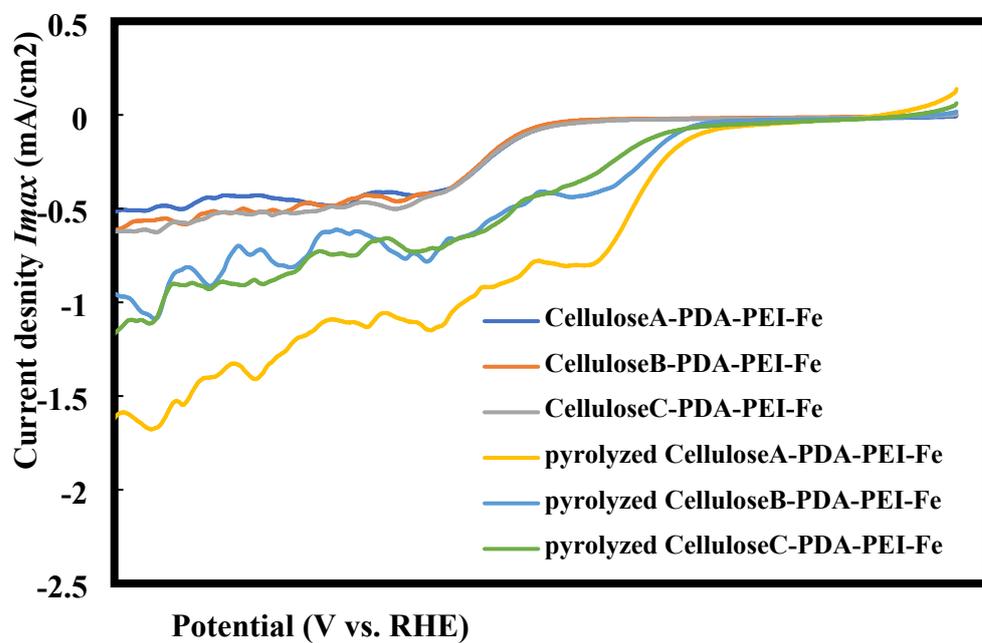




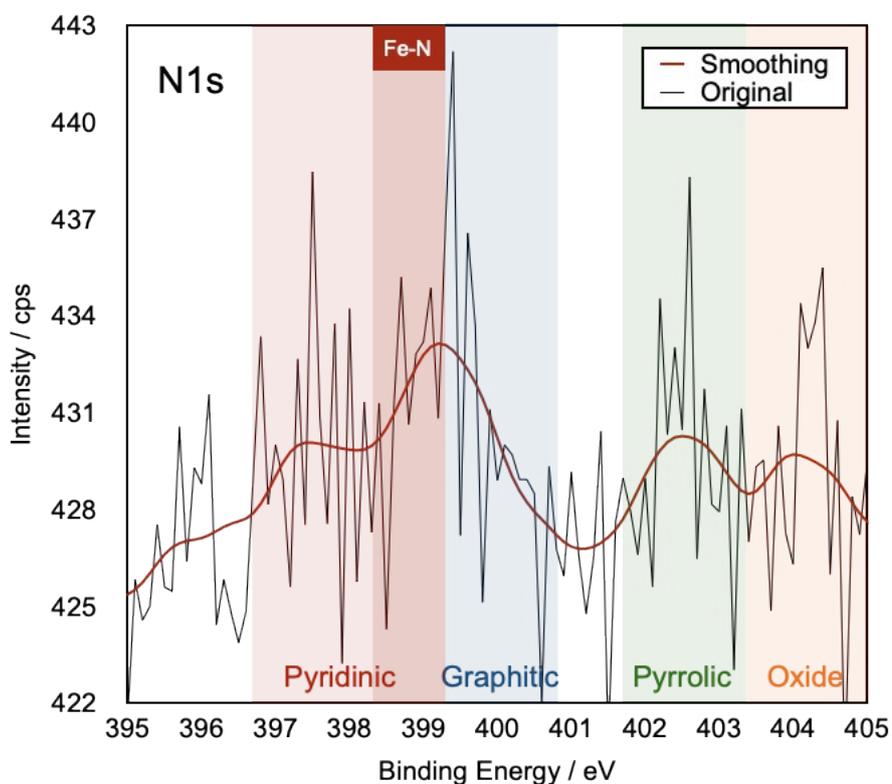
**Figure S7:** LSV curves of Pt/C at 1,600 rpm in O<sub>2</sub>-saturated 0.1 M KOH.

**Table S1: Comparison of electrochemical performance with previous heteroatom doped carbon catalysts in literature.**

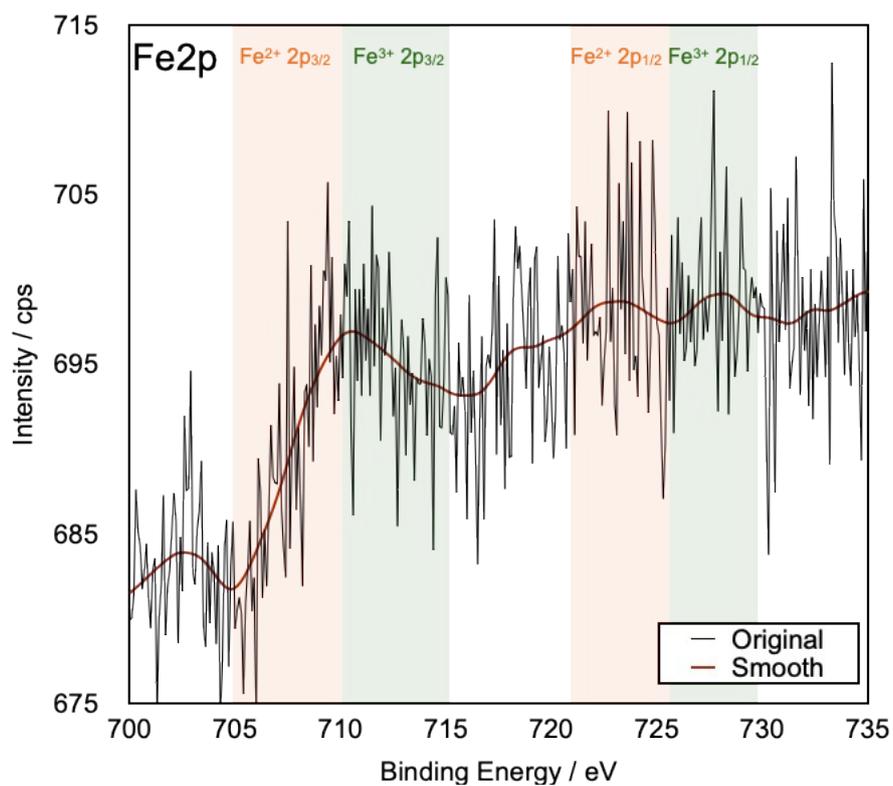
S. No.	Sample	Literature	$V_{onset}$	$I_{max}$	$n$
1	Calcined PDA-PEI-Fe	20	0.914	3.4	3.2
2	pS-PDA	26	0.863	5.6	3.2
3	pS-HPDA	26	0.903	6.1	3.6
4	NBSCP	30	1.01	5	-
5	ANDC-900-10	31	0.84	5.5	-



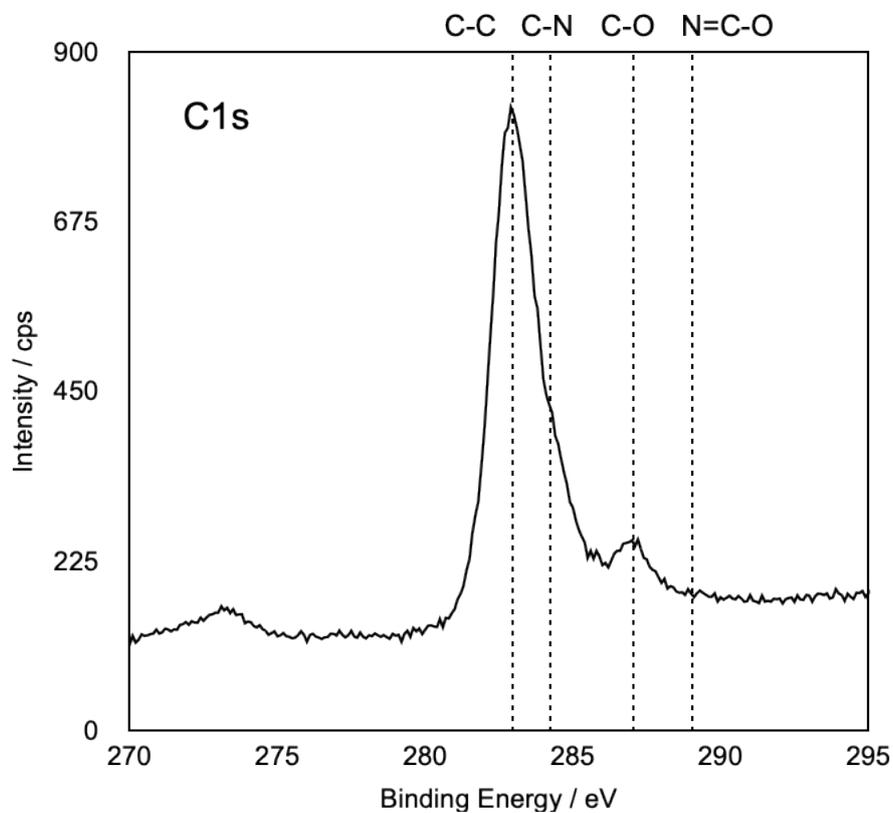
**Figure S8:** LSV curves of pyrolyzed and non-pyrolyzed samples at 0 rpm in O<sub>2</sub>-saturated 0.1 M KOH.



**Figure S9.** High resolution narrow scan original and smoothing XPS spectra of N1s of pyrolyzed CNC-A after PDA-PEI-Fe coating. From the smoothing spectrum, peaks attributed to pyridinic, graphitic, pyrrolic and oxide nitrogen were observed, and there is strong peak attributed to Fe-N pyridinic nitrogen clearly existed at 399 eV. Note that the peak was overlapped both with pyridinic and graphitic nitrogen.



**Figure S10.** High resolution narrow scan original and smoothing XPS spectra of Fe2p of pyrolyzed CNC-A after PDA-PEI-Fe coating. From the smoothing spectrum, peaks attributed to Fe<sup>2+</sup> 2p<sub>3/2</sub>, Fe<sup>3+</sup> 2p<sub>3/2</sub>, Fe<sup>2+</sup> 2p<sub>1/2</sub>, and Fe<sup>3+</sup> 2p<sub>1/2</sub> were clearly found.



**Figure S11.** High resolution narrow scan XPS spectra of C1s of pyrolyzed CNC-A after PDA-PEI-Fe coating. Clear C-C and C-O peaks found and C-N peak was found as a shoulder of the C-C peak, which indicated that formation of nitrogen doped carbon. There was no clear C=N-O peak found.

