

## Supporting Information

### **Iodine-treated heteroatom-doped carbon: conductivity driven electrocatalytic activity**

Kiran Pal Singh, Min Young Song and Jong-Sung Yu\*

Department of Advanced Materials Chemistry, Korea University, 2511 Sejong-ro, Sejong 339-700, Republic of Korea.

**Summary:** This file contains 9 pages, 7 figures and 2 tables

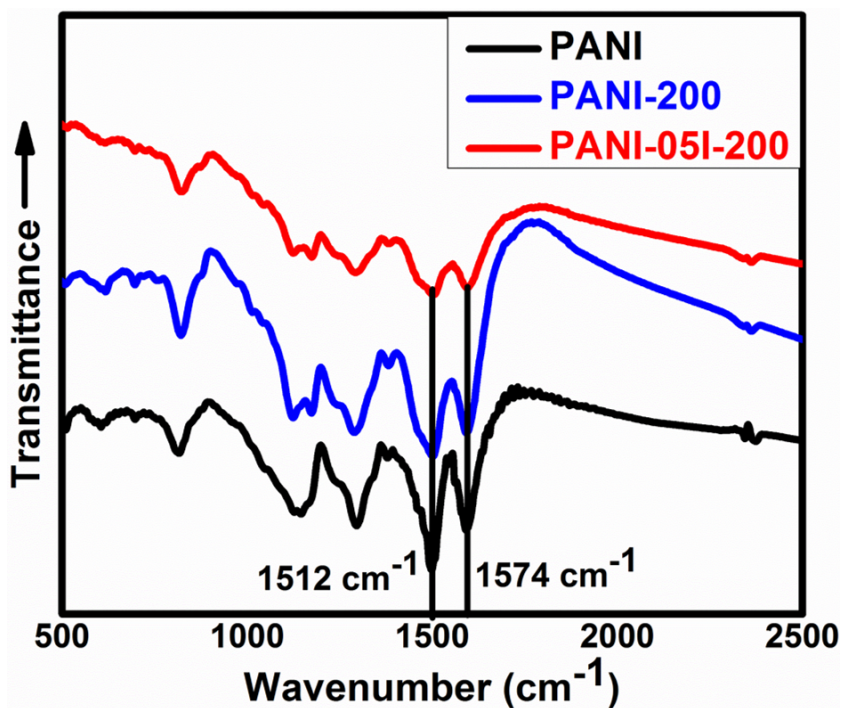


Fig. S1 FTIR spectra of PANI, PANI-200 and PANI-05I-200

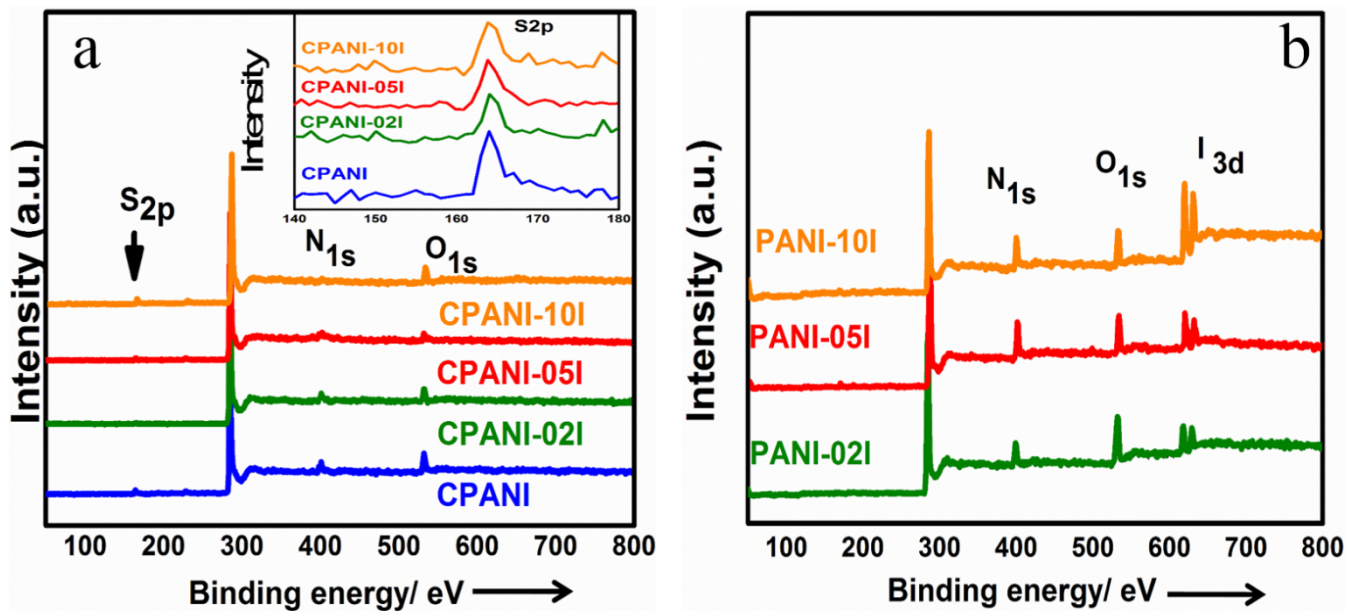
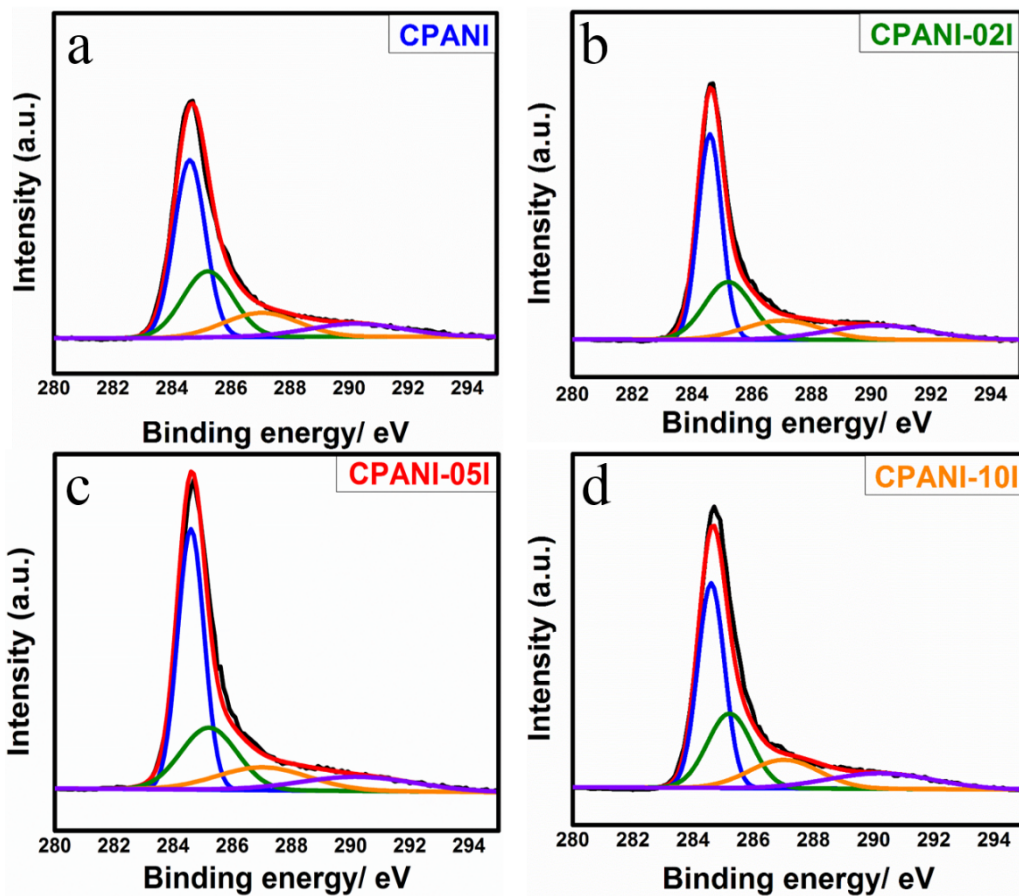
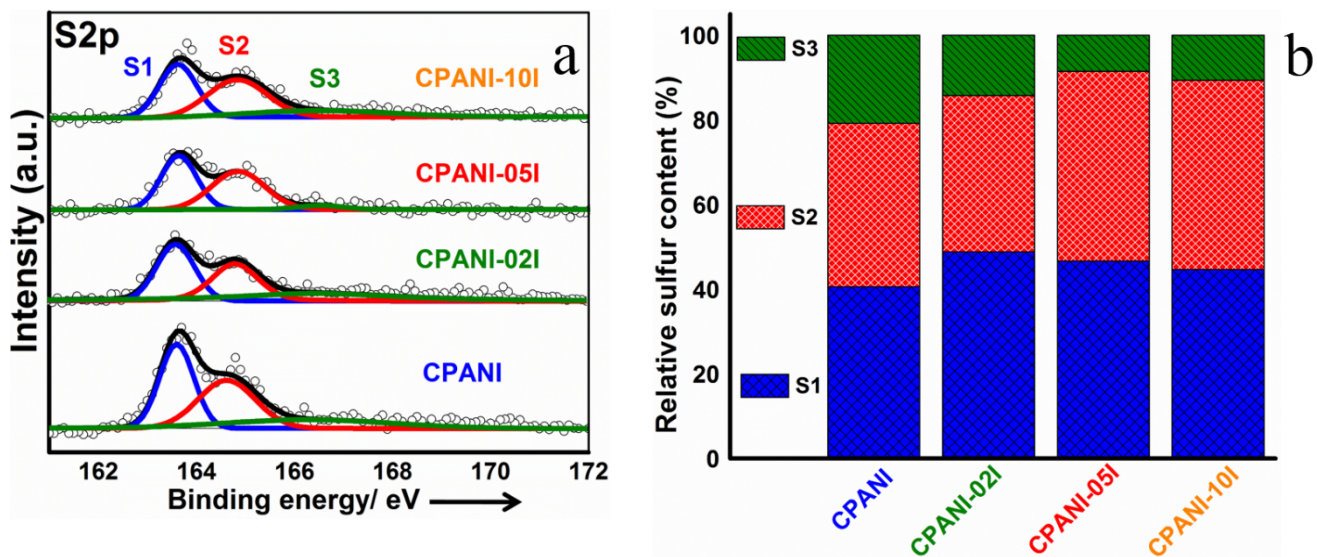


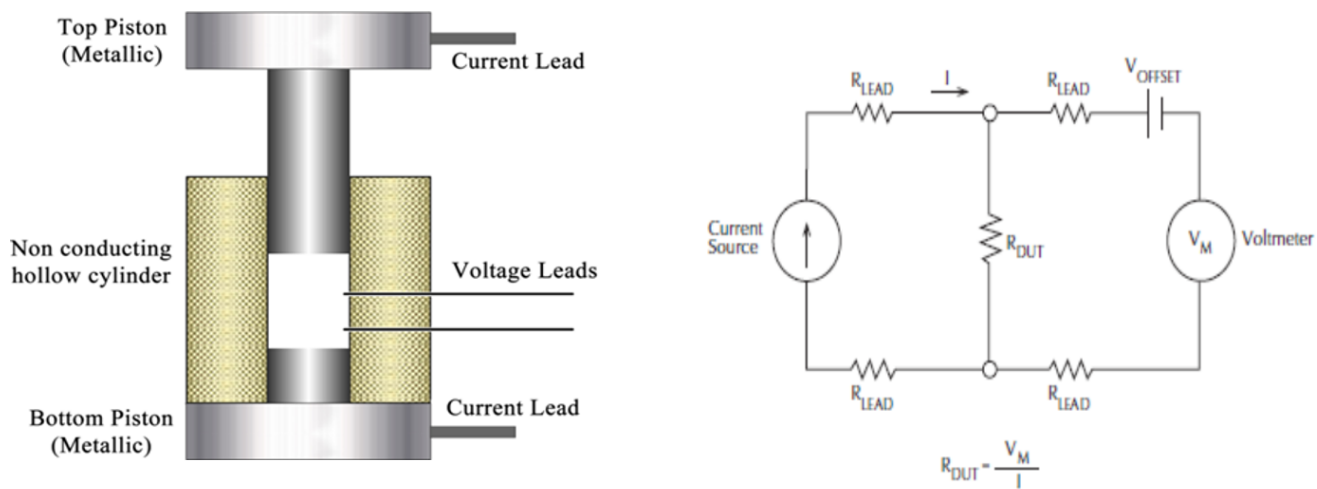
Fig. S2 XPS spectra of a) CPANI, CPANI-02I, CPANI-05I and CPANI-10I and b) PANI, PANI-02I, PANI-05I and PANI-10I.



**Fig. S3** Deconvoluted XPS spectra of C 1s for a) CPANI, b) CPANI-02I, C) CPANI-05I and d) CPANI-10I.

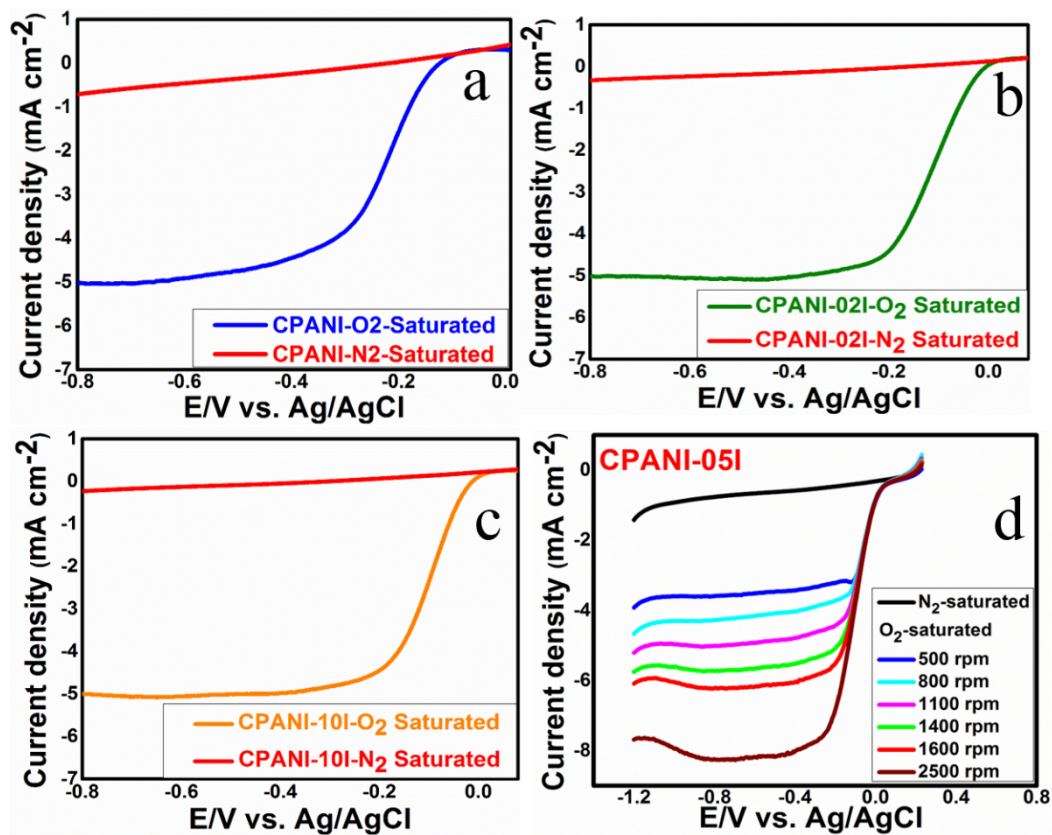


**Fig. S4** (a) Deconvolution of S 2p into three main components, S1: (S P3/2), S2: (S P1/2) and S3: (SOx) and (b) distribution of major components of sulfur present in CPANI, CPANI-02I, CPANI-05I and CPANI-10I.

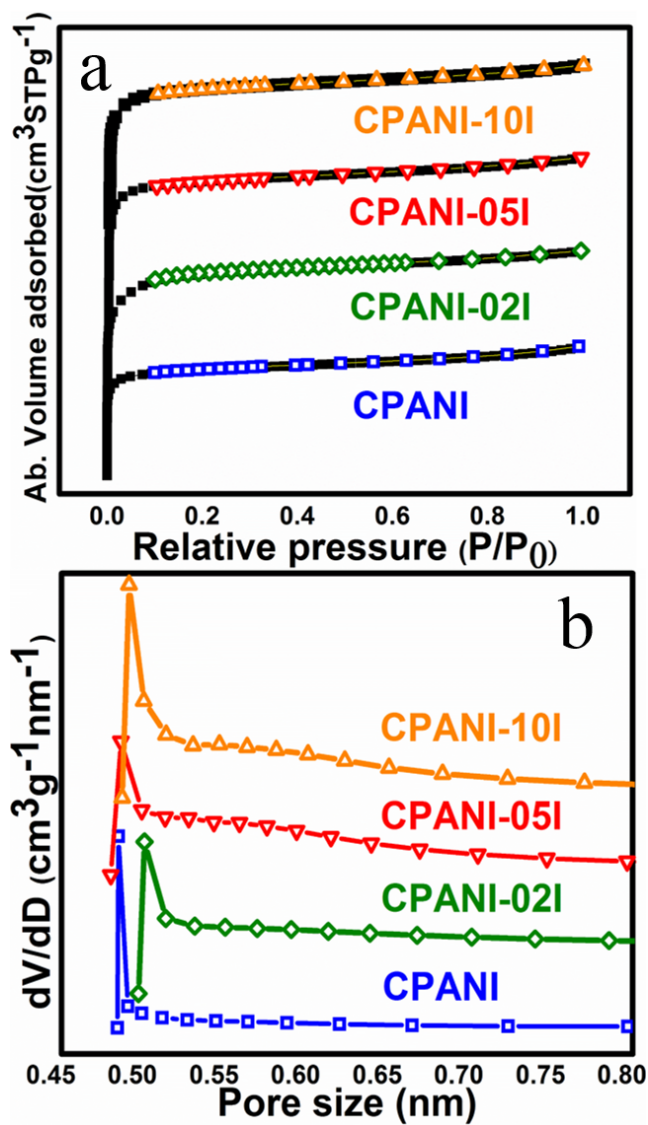


**Fig. S5** Design of four probe apparatus used to measure conductivity of the powder carbon samples and circuit diagram of the resistance measurement technique.





**Fig. S6** Linear sweep voltammetry (LSV) curves of ORR in O<sub>2</sub>- and N<sub>2</sub>-saturated atmosphere at 1600 rpm for (a) CPANI, (b) CPANI-02I and (c) CPANI-10I, and (d) LSV curves of ORR at various rotation rates for CPANI-05I



**Fig. S7** (a) Nitrogen adsorption-desorption isotherms and (b) the corresponding pore size distribution curves of CPANI, CPANI-02I, CPANI-05I and CPANI-10I.

**Table S1** Nitrogen sorption and electrochemical conductivity data of untreated CPANI and I-treated CPANI-02I, CPANI-05I and CPANI-10I

Sample	Physical characteristics					
	BET total surface area (m <sup>2</sup> g <sup>-1</sup> )	Micropore surface area (m <sup>2</sup> g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Micropore volume (cm <sup>3</sup> g <sup>-1</sup> )	H-K pore size (nm)	Conductivity (S/cm) at 18 MPa
CPANI	855	811	0.38	0.36	0.48	6.50
CPANI-02I	1104	1058	0.48	0.42	0.50	14.05
CPANI-05I	1130	1082	0.48	0.41	0.48	19.77
CPANI-10I	1060	1011	0.40	0.38	0.49	17.87

**Table S2** Comparison of ORR activities and kinetics of reported heteroatom-doped carbon catalysts with the iodine treated heteroatom-doped catalyst in this work.

Catalyst	Preparation method/Pyrolysis temperature	Electrolyte	Onset potential (V vs. Ag/AgCl)	Current density (mA/cm <sup>2</sup> )	Peak Potential. (V)	Reference
I-treated heteroatom-doped carbon	Pyrolysis of PANI in presence of iodine at 900 °C	0.1 M KOH	+0.021	5.71	-0.14	This work
N-doped graphene	Annealing of GO/PANI composite at 1000°C	0.1 M KOH	N/A	N/A	-0.22	1
N-doped graphene	Heat treatment of graphite with 4-aminobenzoic acid and polyphosphoric acid/P <sub>2</sub> O <sub>5</sub> at 170° C	0.1 M KOH	-0.13	N/A	N/A	2
Metal-free N-doped carbon aerogels made from ionic liquids	Carbonization of ionic liquid 1-ethyl-3-methylimidazolium dicyanamide mixed with the NaCl/ZnCl <sub>2</sub> at 1000 °C	0.1 M KOH	N/A	~6.0	-0.2	3
S-doped graphene	Annealing of GO and benzyl disulfide at 1050° C	0.1 M KOH	N/A	N/A	-0.29	4
N-S doped graphene	Annealing of melamine/BDS/GO/SiO <sub>2</sub> mixture at 900°C	0.1 M KOH	-0.06	N/A	-0.24	5
N-S doped graphene	Dispersion of GO in thiourea solution which is autoclaved at 180° C. After freeze drying no carbonization was carried out	0.1 M KOH	-0.15	3.9	-0.36	6
N-S doped graphene	GO was heated with 2-aminothiophenol in presence of polyphosphoric acid at 200° C	0.1 M KOH	-0.129 <sup>a</sup>	N/A	-0.40 <sup>a</sup>	7
N-doped carbon from ionic liquids and nucleobases	By heating nonvolatile ionic liquids featuring dicyanamide anions to temperatures of 1000 °C	0.1 M KOH	0.035	N/A	-0.192	8
Edge-halogenated (I) graphene	Ball-milling of graphite in the presence of I <sub>2</sub>	0.1 M KOH	-0.14	N/A	-0.22	9



I-doped graphene	Pyrolysis of GO with I <sub>2</sub> at 1100°C	0.1 M KOH	-0.08	N/A	-0.29	10
Fe containing N-doped carbon	Annealing of iron-complex (derived from bidppz and FeSO <sub>4</sub> ) at 800°C	0.1 M KOH	-0.02 <sup>b</sup>	6.0 <sup>c</sup>	-0.03 <sup>b</sup>	11

All the SCE<sup>a</sup> and RHE<sup>b</sup> potentials have been converted to the Ag/AgCl potential.

C. The corresponding current densities are estimated from figure in reported literature.

#### References:

1. Z. Lin, G. Waller, Y. Liu, M. Liu and C. P. Wong, *Carbon*, 2013, **53**,130.
2. I. Y. Jeon, D. Yu, S. Y. Bae, H. J. Choi, D. W. Chang, L. Dai and J. B. Baek. *Chem. Mater.*, 2011, **23**, 3987.
3. K. Elumeeva, N. Fechler, T. P. Fellingner and M. Antonietti. *Mater. Horiz.*, 2014, Advance Article.
4. Z. Yang, Z. Yao, G. Li, G. Fang, H. Nie, Z. Liu, X. Zhou, X. Chen and S. Huang. *ACS Nano*, 2012, **1**, 205.
5. J. Liang, Y. Jiao, M. Jaroniec, S. Zhang and S. Z. Qiao, *Angew. Chem. Int. Ed.*, 2012, **51**, 11496.
6. Y. Su, Y. Zhang, X. Zhuang, S. Li, D. Wu, F. Zhang and X. Feng, *Carbon*, 2013, **62**, 296.
7. Z. Zuo, W. Li and A. Manthiram, *J. Mater. Chem. A*, 2013, **1**, 10166.
- 8 W. Yang, T.-P. Fellingner, and M. Antonietti, *J. Am. Chem. Soc.*, 2011, **133**, 206.
9. I. Y. Jeon, H. J. Choi, M. Choi, J. M. Seo, S. M. Jung, M. J. Kim, S. Zhang, L. Zhang, Z. Xia, L. Dai, N. Park and J. B. Baek, *Sci. Rep.*, 2013, **3**, 1810.
10. Z. Yao, H. Nie, Z. Yang, X. Zhou, Z. Liu and S. Huang, *Chem. Commun.*, 2012, **48**, 1027.
11. L. Lin, Q. Zhu and A. W. Xu, *J. Am. Chem. Soc.*, 2014, **134**, 11027.