Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Solution Plasma Synthesis Process of Tungsten Carbide on N-doped Carbon Nanocomposite with Enhancing Catalytic ORR Activity and Durability

Dae-wook Kim,*[a] Oi Lun Li,[b] Panuphong Pootawang,[b] Nagahiro Saito[a,b,c]

[a] Department of Materials, Physics and Energy Engineering, Nagoya University, 464-8603, Furo-cho, Chikusa-ku, Nagoya, Japan.
[b] Green Mobility Collaborative Research Center, Nagoya University, 464-8603, Furo-cho, Chikusa-ku, Nagoya, Japan.
[c] EcoTopia Science Institute, Nagoya University, 464-8603, Furo-cho, Chikusa-ku, Nagoya, Japan

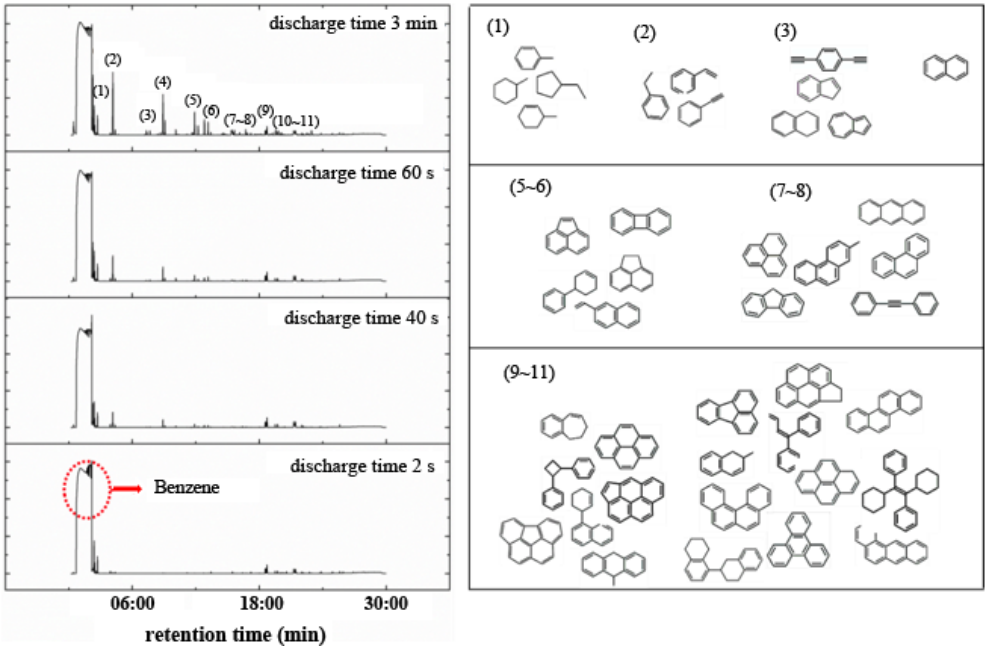

Fig. S1 Chromatograms of the discharged solution (benzene) by SPP with chemical formulas.

Table S1 Compound name corresponding to the Chromatograms (Fig. S1)

Group	Compound	
1	Cyclohexane, methyl-	Cyclopentane, ethyl-
	Cyclohexane, 3-methyl-	Toluene
2	Ethylbenzene	Phenylethyne
	Styrene	
3	Indene	1,4-Diethynylbenzene
	Azulene	
4	Naphtalene	1,4-Diethynylbenzene
5~6	Biphenyl	Naphtalene, 2-ethenyl-
	Biphenylene	Acnaphthene
	Acenaphthylene	Styrene
7~8	Benzene, 1,1'-(1,2-cyclobutanediyl)bis,trans-	Benzene, 3-cyclohexen-1-yl
	Fluorene	1H-Phenalene
	Anthracene	Phenanthrene
	Diphenylacetylene	[2,2]Paracyclophane
	Naphthalene, 1,2,3,4-tetrahydro-2phenyl-	Cyclobutan, 1,3-diphenyl-trans-phane
	Benzene, 3-cyclohexen-1-yl-	
9~11	Anthracene, 9-methyl-	Phenanthrene, 2-methyl-
	Anthracene	Benzene, 1,1'-(1,2-cyclobutanediyl)bis-,cis-
	5H-Benzocycloheptene, 6,7-dihydro-	Benzene, 1,3-hexadienyl-
	1,4-Dihydronaphthalene	Benzene, 1,1'(1,3-butadiyne-1,4-diyl)bis-
	Fluoranthene	Pyrene
	Triphenylene	Pyrene, 4,5-dihydro-
	Annulene	Benzo[ghi]fluoranthene
	Benzo[c]phenanthrene	Cyclopenta[cd]pyrene
	Benzo[a]anthracene	Chrysene
	Cyclopenta[cd]pyrene	Cyclopenta[cd]pyrene, 3,4-dihydro-

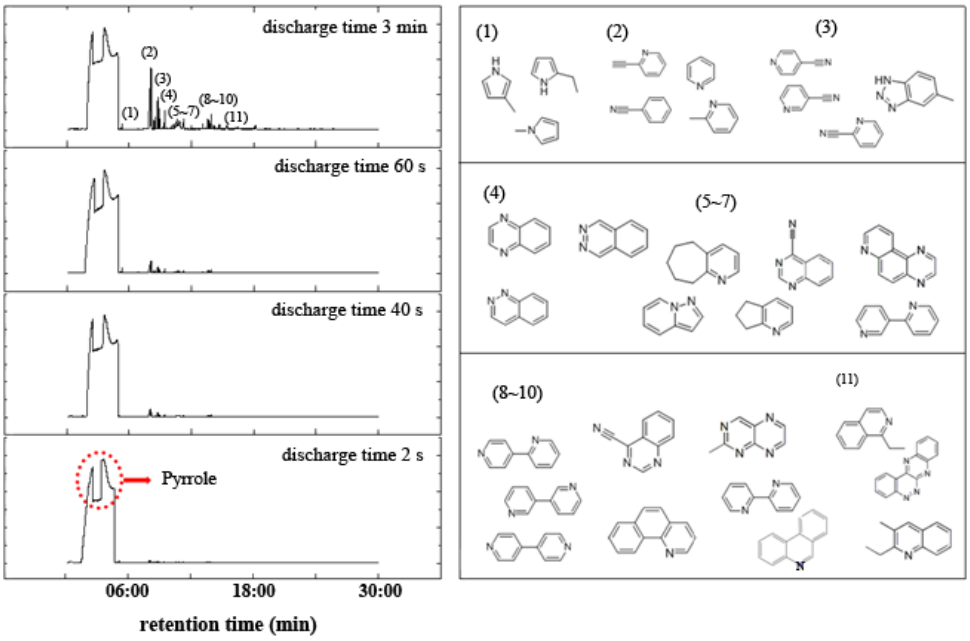

Fig. S2 Chromatograms of the discharged solution (pyrrole) by SPP with chemical formulas.

Table S2Compound name corresponding to the Chromatograms (Fig. S2)

Group	Compound	
1	1H-Pyrrole, 3-methyl-	1H-Pyrrole, 2-methyl-
	1H-Pyrrole, 1-methyl-	
2	Pyridine	Pyridine, 2-methyl-
	2-Ethynylpyridine	Bezonitrile
3	4-Pyridinecarbonatrile	3-Pyridinecarbonatrile
	2-Pyridinecarbonatrile	Benzenemathanimine
	1H-Benzotriazole, 5-methyl-	
4	Cinnoline	quinoxaline
	Phthalazine	1H-Benzotriazole, 5-methyl-
5~7	5H-1-Pryydine, 6,7-dihydro-	Pyrazolo[1,5-A]pyridine
	4-Cyancinnoline	Benzene, 3-cyclohexen-1-yl
	Pyrido[3,2-f]quinoxaline	4-Cyancinnoline
	2,3-Cycloheptenopyridine	2,3'-Dipyridyl
	Pyrido[3,2-f]quinoxaline	
8~10	2,2'-Bipyridine	2,4'-Bipyridine
	4,4'-Bipyridine	3,3'-Bipyridine
	Benzo[c]cinnoline	Benzo[h]cinnoline
	Benzo[h]quinazoline	Pteridine, 2-methyl-
	Quinazoline-4-carbonitrile	1H-indole-3-acetonitrile
11	Quinoxalino[2,3-c]cinnoline	Pteridine, 2-methyl-
	Quinoline, 2-ethyl-3-methyl-	Isoquinoline, 1-ethyl-
	Benzo[h]cinnoline	

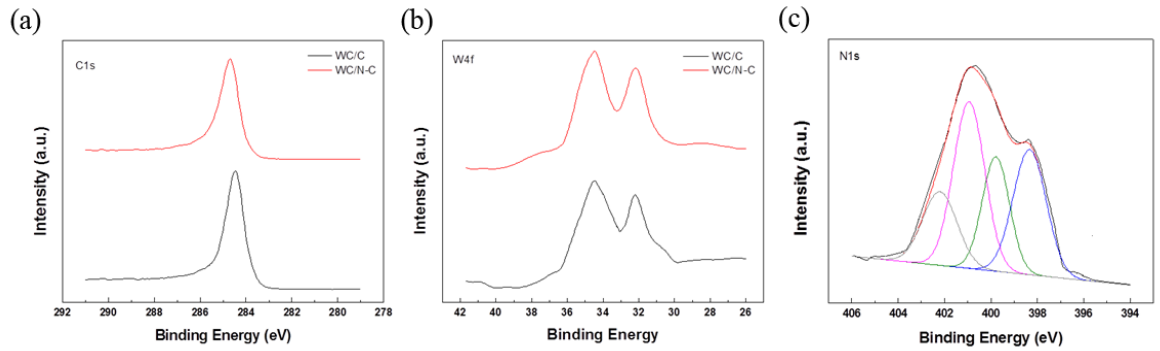

Fig. S3 XPS spectra (a) C1s, (b) W4f, (c) N1s

Fig. S3(a) shows C1s spectra of the WC/C nanocompsite with and without nitrogen contents. The main peak of t he C1s spectra at 284.4 and 284.8 eV, respectively, which are originated from sp2 C-C bond in carbon structure [1]. In case of WC/N-C, the main peak was positively shifted, and which is promoted by presence of nitrogen co mponents in the carbon matrix. [2]. On the W4f spectra, the results are quite similar to each others. It show only WC related peak at 34.4 and 32.1 eV without the effect of the support materials. The N1s spectra of WC/N-C, ty pical peaks of 4 type of nitrogen bonding (pyridinic-N (398.3 eV), pyrrolic-N (399.8 eV), graphtic-N (401.1 eV), and oxidized-N (402.2 eV)) were observed. From the obtained results, it assumes that the nitrogen components were well incorporated in the carbon matrix.

Table S3 Calculated particle size of WC nanoparticles from XRD

Crystallite size (nm)								Mean crystallite size (nm)			
Plane	WC_{1-X} (As-prepared)		WC_{1-X} (Heat-treated)		Plane	WC (Heat-treated)		WC_{1-X} (As-prepared)		WC & WC_{1-X} (Heat-treated)	
	WC/C	WC/N-C	WC/C	WC/N-C		WC/C	WC/N-C	WC/C	WC/N-C	WC/C	WC/N-C
(111)	4.17	4.03	7.78	8.37	(001)	9.49	9.81	4.58	4.56	6.78	6.76
(200)	4.30	4.51	6.15	5.76	(100)	6.52	5.60				
(220)	5.57	5.42	6.67	5.99	(101)	5.54	5.90				
(311)	4.28	4.32	6.98	7.79	(110)	5.25	6.16				
					(111)	6.72	5.32				

Reference

1. S. Maldonado, S. Morin, K. J. Stevenson, *Carbon*, 2006, **44**, 1429–1437.
2. P. Ayala, A. Grüneis, T. Gemming, B. Büchner, M. H. Rümmeli, D. Grimm, *Chem Mater*., 2007, **19**, 6131–6137.