Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A
This journal is © The Royal Society of Chemistry 2014

Supporting Information

Highly stable electrocatalysts supported on nitrogen-self-doped three-dimensional graphene-like networks with hierarchical porous structure

Juhong Cheng,[a] Yunyong Li,[a] Xiangdong Huang,*[b] Qingquan Wang,[b] Ao Mei,[b] Pei Kang Shen,*[a]

a State Key Lab oratory of Optoelectronic Materials and Technologies, School of Physics and Engineering, Sun Yat-sen University, 135 Xingang Road, Guangzhou,510275, PR China. E-mail : stssp k@mail.sysu .edu.cn; Fax: +86-20-84036736; Tel:+86-20-84036736

b Automotive Engineering Institute, Guangzhou Automobile Group Co., Ltd, Guangzhou, 510640, PR China. E-mail : huangxd@gaei.cn

Synthesis of 3D-GNs

For the preparation of nitrogen-free three-dimensional graphene-like networks (denoted as 3D GNs), 10 g pretreated macroporous acrylic type cation-exchange D113 resin was firstly impregnated with 100 mL 0.05 mol L^{-1} of $Co(NO_3)_2$ solution, then the dried exchanged resin was added into 400 mL KOH/ethanol solution containing 15 g KOH for activation. Finally, the mixture was heated at 850 ^oC for 2 h in N_2 atmosphere with a heating rate of 2 ^oC min^{-1}. The 3D GNs was further treated with HCl solutions, washed by deionized water and dried at 120 ^oC for 5 h.

Synthesis of C-Pristine

10 g pretreated macroporous acrylic type cation-exchange D113 resin was directly heated at 850 ^oC for 2 h in N_2 atmosphere. After cooling down to room temperature, the C-Pristine was washed by deionized water and then dried at 120 ^oC for 5 h.

Synthesis of Pt/N-3D GNs, Pt/3D GNs and Pt/C-Pristine

In a typical synthesis, 3 ml (15 mgPt ml^{-1}) chloroplatinic acid was well mixed with ethylene glycol (EG, 50 ml) in an ultrasonic bath. Then, the N-3D GNs (or 3D GNs and C-Pristine, 55 mg) was added into the mixture. The pH of the mixture was adjusted to 10 by a dilute KOH/EG solution. The mixture

was microwave-heated in the form of 5 s-on/5 s-off for several times. The resulting black solid sample was acidified, filtered, washed and dried at 80 °C for 12 h in a vacuum oven.

Table S1 Resistivity under different pressure of various supporting materials

Samples	Resistivity under different pressure/ (Ω*cm)				
	1MPa	2MPa	4MPa	6MPa	8MPa
C-Pristine	5.21	2.70	1.536	1.113	0.880
N-3D GNs	0.394	0.255	0.180	0.148	0.126
3D GNs	0.373	0.239	0.169	0.136	0.114

Table.S2 surface area and pore structure summary of N-3D GN, Pt/N-3D GNs, 3D GNs, and C-Pristine

Samples	S_{BET}	$V_{0.98t}$[a]	V_{mi}[b]	V_{mea}[c]
	(m^2/g)	(cm^3/g)	(cm^3/g)	(cm^3/g)
C-Pristine	137.8	1.999	0.0421	0.1578
3D GNs	729	0.5393	0.3003	0.2390
N-3D GNs	745	0.6018	0.2214	0.3804
Pt/N-3D GNs	511	0.4709	0.2027	0.2682

[a] Single point desorption to total pore volume of pores at $P/P_0 = 0.98$.
[b] t-Plot micropore volume.
[c] Mesopore and macropore volume obtained by subtracting V_{mi} from $V_{0.98t}$.

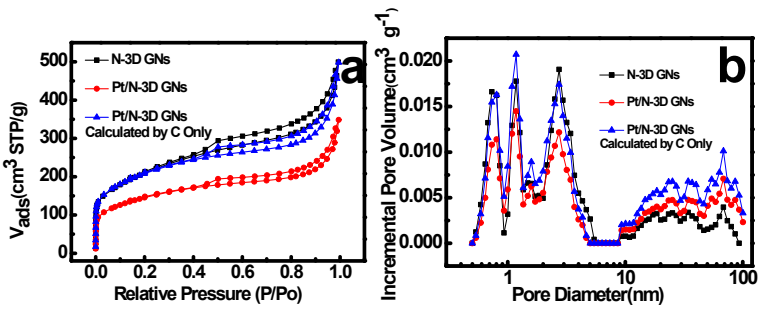

Fig.S1. Nitrogen adsorption/desorption isotherms (a) and DFT pore-size distribution curves (b) of N-3D GNs, Pt/N-3D GNs and Pt/N-3D GNs Calculated by C Only.

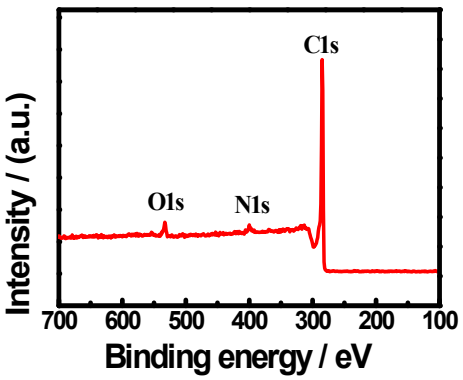

Fig.S2. XPS spectrum of N-3D GNs

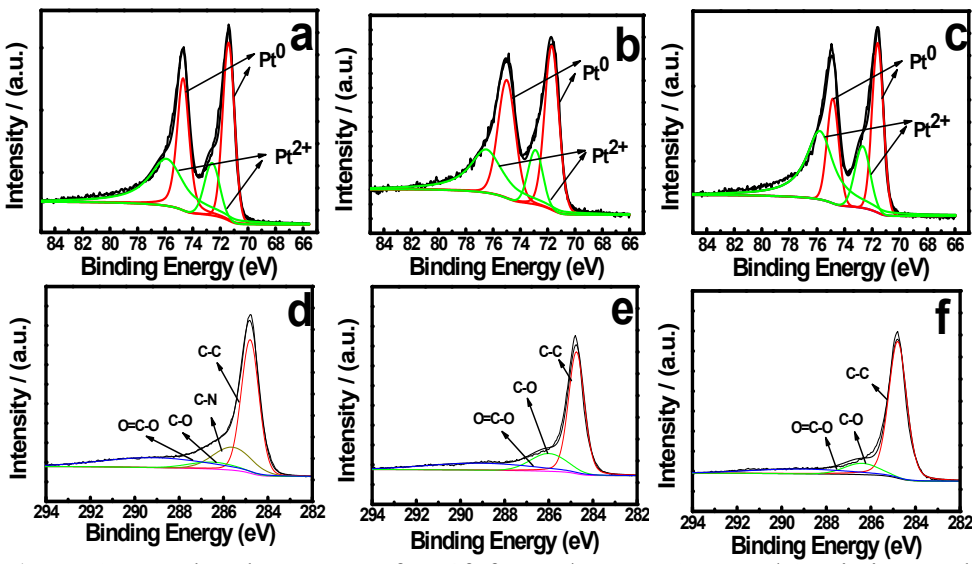

Fig.S3 (a, b, c) XPS core level spectra of Pt4f for Pt/N-3D GNs, Pt/C-Pristine and Pt/3D GNs, respictively; (d, e, f) XPS core level spectra of C1s for Pt/N-3D GNs, Pt/C-Pristine and Pt/3D GNs, respictively.

Table S3 Summary of position and assignments of C, Pt, and N components of the Pt/C-Pristine, Pt/3D GNs and Pt/N-3D GNs samples

	Pt/C-Pristine			**Pt/3D GNs**			**Pt/N-3D GNs**		
	Position	Attribution	Percentage	Position	Attribution	Percentage	Position	Attribution	Percentage
C	284.6	C-C	75.9	284.6	C-C	60.6	284.6	C-C	63.4
	286.5	C-O	10.7	286.5	C-O	18.3	285.6	C-N	10.4
	289.1	O=C-O	13.4	289.1	O=C-O	21.1	286.5	C-O	6.5
							289.1	O=C-O	19.7
Pt	71.6	$Pt^0(4f_{7/2})$	45.5	71.6	$Pt^0(4f_{7/2})$	55.2	71.6	$Pt^0(4f_{7/2})$	61.1
	74.8	$Pt^0(4f_{5/2})$		74.8	$Pt^0(4f_{5/2})$		74.8	$Pt^0(4f_{5/2})$	
	72.4	Pt^{2+}	54.5	72.4	Pt^{2+}	44.8	72.4	Pt^{2+}	38.9

	76	Pt^{2+}		76	Pt^{2+}	76	Pt^{2+}
N						398.5	Pyridine N 45.9
						400.2	Pyrrole N 30.1
						401.1	Graphtic N 24