Supporting information

Surface Modified Single Wall Carbon Nanohorn as an Efficient Electrocatalyst for Platinum-Free Fuel Cell Cathode

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Experimental

Synthesis of FeNC

For the preparation of the Fe coordinated nitrogen doped carbon (FeNC) samples, we have used Vulcan carbon mixed with melamine and FeCl₃ (amounts were taken as similar to the case of FeNCNH). The adopted synthesis procedures were similar to that used for preparing FeNCNH. The annealing was done at 900 °C under argon atmosphere for 3 h.

Synthesis of Fe complex on SWCNH

For the Fe complex synthesis, we have followed the procedure reported by Thorum et al (Angew. Chem. Int. Ed, 2009, 48, 165). In a typical synthesis, FCNH and FeCl₃ were mixed well in deionized water. 0.159 g of 3.5 diamino-1,2,4-triazole in 10 ml solution was added slowly in to the above mixture and the mixture was stirred for 18 h. After stirring, the solid material was collected using filtration and it was dried under vacuum at 80 °C for overnight.

Physical characterizations

X-ray diffraction (XRD) patterns were obtained from PANalytical X'pert Pro instrument. Cu K α (1.5418 Å) radiation was used for the X-ray radiation. Raman analyses of the samples were carried using HR 800 Raman spectrometer (Jobin Yvon, Horiba, France) using 632.8 nm green laser (NRS 1500 W). High resolution transmission electron microscope (HR-TEM) FEI model (TECNAI G2 F30) operated at an

accelerating voltage of 300 kV (Cs = 0.6 mm, resolution 1.7 Å) and field emission scanning electron microscope (FE-SEM) model NOVA Nano SEM 450, were used for analyzing morphology of the synthesized materials. X-ray photoelectron spectroscopy (XPS) analysis was carried out using a VG Microtech Multilab ESCA 3000 spectrometer equipped with an Al K α X-ray source. Electrical conductivity of SWCNH and NCNH were measured using the four probe technique. The measured values are respectively 6.5 S/cm and 9.2 S/cm.

Electrochemical Characterization

Electrochemical studies of the samples were carried out in a Biologic electrochemical work station with a three-electrode test cell from Pine Instruments. Oxygen and nitrogen saturated 0.1 M KOH was used in the electrochemical experiments as the electrolyte. Hg/HgO was used as the reference electrode and a glassy carbon rod was used as the counter electrode. A glassy carbon (GC) electrode (5 mm diameter) from Pine Instruments was used as the working electrode (WE) after drop coating the samples. To prepare the catalyst slurry for the electrochemical analysis, 5 mg of the catalyst dispersed in 1 ml of N, N-dimethyl acetamide solution by sonication. 20 μ L catalyst slurry was drop-coated on the electrode followed by 2 μ L of 0.1 % Nafion® solution was applied on catalyst layer. 100 μ g was the total catalyst loading on the electrode. Liner sweep voltammogram (LSV) was recorded in oxygen saturated 0.1 M KOH solution at a scan rate of 5 mV s⁻¹ at different electrode rotation rates varied from 400 to 2500 rpm. The Koutecky-Levich (K-L) plot, a plot of inverse of current versus inverse of electrode rotation at different potential, was used to calculate the number of electrons. Slope and Y-intercept were used to calculate the kinetic current density and number of electron transfer respectively. The number of electron transfer during ORR was calculated using the equation:

$$B = 0.6 \text{ nFv}^{-1/2}C_{O2}D_{O2}^{2/3}$$

where 'n' is the electron transfer number, 'F' is the Farady constant (96486 C mol⁻¹), 'C₀₂' is the concentration of oxygen in 0.1 M KOH (1.2 X 10⁻³ mol l⁻¹), 'D₀₂' is the diffusion coefficient of oxygen in 0.1 M KOH solution (1.9 X 10⁻⁵ cm s⁻¹) and 'v' is the kinematic viscosity.

Double layer capacitance of the materials was calculated from the cyclic voltammogram performed in N_2 saturated 0.1 M KOH at a scan rate of 50 mV/s. The equation used for the calculation of capacitance is given below:

$$C(F/g) = \frac{i}{\vartheta * m}$$

Electrocatalyst	Capacitance (F/g)
FeNCNH-900	420
FeNCNH-800	540
FeNCNH-1000	560
Fe Complex	198
FeCN	97
NCNH	288

where 'C' is specific capacitance, 'i' current, 'v' is scan rate and 'm' is the loading of catalyst material.

Anion exchange membrane fuel cell test

Fumapem FAA membrane (FumaTech, Germany) was used as the anion exchange membrane. The membrane was pretreated using the following procedure. The membrane was soaked in 1 M KOH for 24 h to replace bromide by OH⁻. Subsequently, the membrane was washed by using deionized water. The thickness of the membrane at wet condition was 65 μ m. Conventional brush coating method was applied to make the cathode layer using a slurry of FeNCNH-900 and 10 wt. % Fumion in N-methyl pyrrolidone (NMP) with a Fumion to carbon ratio (F/C) of 0.8 in isopropyl alcohol (IPA). A catalyst loading of 4 mg cm⁻² was used on a gas diffusion layer (GDL, SGL CC, Germany). At the anode, 40 wt. % Pt/C (E-TEC) was used with 0.5 mg cm⁻² (F/C is 0.4) catalyst loading. For comparison, the cathode layer was also made

with 40 wt. % Pt/C (E-TEC) with a Pt loading of 0.8 mg cm⁻² and an F/C ratio of 0.4. Membrane electrode assembly (MEA) was prepared by keeping the membrane in between the cathode and anode followed by applying 0.5 ton pressure for 30 sec at room temperature. Active electrode area of the MEA was 4 cm². A standard test fixture from Fuel Cell Technologies, Inc, USA, was used for the single cell analysis. The testing was done by using a fuel cell test station (Fuel Cell Technologies, Inc, USA) by purging H₂ with a flow rate of 50 sccm at the anode and O₂ with a flow rate of 100 sccm at the cathode by maintaining a relative humidity of 100 % and a cell operating temperature of 50 °C.



Figure S 1. FE-SEM images (a & b) and the corresponding elemental mapping of carbon, nitrogen, iron and oxygen in FeNCNH-900.



Figure S2. (a) X-ray diffraction patterns of FeNCNH-900, NCNH and SWCNH.



Figure S 3. LSVs of the different electrocatalysts recorded in oxygen and nitrogen saturated 0.1 M KOH solution. The potential at which the deviation in the current density of LSV in oxygen saturated case occurs has been considered as the onset potential for ORR.



Figure S 4. (a) K–L plots of FeNCNH-900, NCNH and FeCN at a potential of -0.3 V vs. Hg/HgO and (b) the plot of the number of electrons transferred vs. the potential as calculated from the KL plots.



Figure S 5 LSVs of (a) FeNCNH-800, (b) FeNCNH-900 and (c) FeNCNH-1000 at different rotation speed in 0.1 M oxygen saturated KOH at a rotation speed of 1600 rpm and a scan rate of 5 mV s⁻¹.



Figure S 6 j_k vs. E plot; j_k was calculated from the intercept of the K-L plots of FeNCNH-800, FeNCNH-900 and FeNCNH-1000.



Figure S 7. XPS spectra of Fe in FeNCNH-800, FeNCNH-900 and FeNCNH-1000 samples.



Figure S 8. Deconvoluted XPS spectra of C 1s in NCNH, FeNCNH-800, FeNCNH-900 and FeNCNH-1000 samples.



Figure S 9. Percentage of different types of nitrogen as well as the total nitrogen content of NCNH, FeNCNH-800, FeNCNH-900, and FeNCNH-1000.



Figure S 10. Methanol crossover study of FeNCNH-900 (a) and Pt/C (b) with an electrode rotation rate of 1600 rpm at and a scan rate of 5 mV s⁻¹. 3 M methanol was added into 0.1 M KOH electrolyte to evaluate the crossover effect.



Figure S 11 LSVs of Pt/C before and after ADT in oxygen saturated 0.1 M KOH at an electrode rotation speed of 1600 rpm and a scan rate of 5 mV s ⁻¹ respectively. Hg/HgO and glassy carbon were used as the reference and counter electrode respectively.

		Material	Catalyst	Onset	Pt loading	Over
			loading and	potential	(µg cm ⁻²)	potential
			scan rate			compared to
			scan rate			Pt/C
1	Wu <i>et al^[51]</i>	Fe ₃ O ₄ /N-	51 μ g/cm ² ,	-0.19V vs	51	0.15V (Pt onset
	J. Am. Chem.	GAs	10 mV/s	Ag/AgCl		is not given.
	Soc., 2012 , <i>134</i> ,	GIN	10 111 (75	115/11501		Compared with
	9082					their own ACS
						nano Paper)
	-					
2.	Parvez <i>et</i>	NG/Fe	50.91	-0.04V vs	50.91	0 V
	al ^[S2]		$\mu g/cm^2$, 10	Ag/AgCl		
	ACS Nano					
	2012, 6, 9541		mv/s			
3.	Yin et al ^[S3]	Fe _x N/NGA	51 μ g/cm ² ,	0 V vs	51	0V
	Adv. Funct.		10 mV/s	Δα/ΔαC1		
	Mater. 2014 , 24,		10 111 \$	Ag/AgCI		
	2930 Viena et	C COP D Ea	200 ug/am^2	0.09 V va	200	0.1/
4.		C-COP-P-Fe	$200 \mu\text{g/cm}^2$,	0.98 V VS	200	0 V
	al ^[34]		5 mV/s	RHE		
	Angew. Chem. Int Ed 2014					
	53, 2433					
5.	Hu et al ^[S5]	Fe ₃ C/C-800	600 $\mu g/cm^2$,	1.05 V vs	50	0 V
	Angew. Chem.					
	Int. Ed. 2014,					

Table SI 1. Onset potential ORR of some of the non-precious electrocatalyst recently reported.

	53, 36753		10 mV/s	RHE			
6	Dai <i>et al^[S6]</i>	Functionaliz	10µg,	-0.12V	VS	Not given	0.09V
	ACS Nano 2011, 5, 6202	ed graphene	10mV/s	SCE			
7	Liang <i>et</i>	Fe-N-CNT-	80 µg , 5	Not given		80 µg	0.018V
	al ^[S7]	OPC	mV/s				
	DOI:						
	10.1002/adma.2						
	01401848						
8	Dai <i>et al^[S8]</i>	SN-OMC-4	$306 \ \mu g/cm^2$,	-0.05V	VS	Not given	0.01V
	ACS Appl.		10 mV/s	$\Lambda \alpha / \Lambda \alpha C1$			
	Mater.		10 111 V/S	Ag/AgCI			
	Interfaces 2013,						
	5, 12594–12601						
9	Cho <i>et al^[S9]</i>	Fe/Fe ₃ C	286 $\mu g/cm^2$,	-0.02V	VS	9.5 and 28.6	0.07V
	Angew. Chem.	functionalize	10 mV	Ha/HaO			
	Int. Ed. 2013,	d melamine	10 111 V				
	52, 1026						
10	Present	FeNCNH-	500 μg/ cm ² , 5	0.1V	VS	60	0.03 V more
	work	900	mV/s	Hg/HgO			positive than
							Pt/C

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