Supporting Information:

Prussian blue as a single precursor for synthesis of Fe/Fe₃C encapsulated N-doped graphitic nanostructures as bi-functional catalysts

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Experimental section:

Here, we take commercially available Prussian blue (PB), Iron (III) ferrocyanide $(Fe^{III}_4[Fe^{II}(CN)_6]_3)$ as an single source precursor for the synthesis of N-doped graphene wrapped Fe-Fe₃C hybrid nanostructures by pyrolysis in a closed system without any inert gas flow. We take quartz tube of 1.0 cm diameter with one end closed for pyrolysis. We take the PB (0.5 g) in the tube and the open end was closed by rubber bladder. We, then, pyrolize the PB at different temperatures between 750 to 1050 °C for 2 h. Schematic of the experimental set-up was shown below;



Fig 1. Schematic of the experimental set-up and photographic images of PB before and after annealing.

Preparation of N- doped hollow graphene (N-HG) hybrid:

We take N-doped graphene encapsulated Fe-Fe₃C hybrid nanostructures and treat in concentrated hydrochloric acid solution for overnight followed by washing with Millipore water/ethanol several times and dried at 80 ^oC.

Physical characterizations

Powder X-ray diffraction (XRD) technique were performed with PAN analytical instrument using a Cu K_{α} (λ = 1.54 Å) radiation source. The Raman scattering measurements of all the sample were performed on a Raman system (WITec) with confocal microscopy at room temperature by using a Nd:YAG laser (532 nm) as an excitation source. Field emission Scanning electron microscope (FE-SEM) images and Energy-dispersive X-ray spectroscopy (EDS) were taken on a FE-SEM, FEI-INSPECTF50 instrument by FEI technology. Transmission electron microscope (TEM) and high resolution TEM (HRTEM) images were obtained with a TEM, JEOL- JEM-2100F and selected area electron diffraction (SAED) pattern operated a 200kV accelerating voltage. The TEM sample was prepared by dispersing the sample in ethanol solution by ultrasonic bath and drop-casted on carbon coated cupper grid, and then dried for TEM analysis. The X-ray photoelectron spectroscopy (XPS) was performed for the elemental analysis which were carried out on an ESCALAB 250 (Thermo Electron) with a monochromatic Al K_{α} (1486.6 eV) source. The surface atomic concentrations were determined from

photoelectron peaks areas using the atomic sensitivity factors reported by Scofield. The binding energy was calibrated by placing the principal C1s peak at 284.6 eV.

Electrochemical measurements:

Electrochemical measurements were conducted using electrochemical work station with rotating disk electrode and Bipotentiostat (CH Instruments). Each time hybrid catalyst ink were prepared by ultrasonically dispersed 5 mg catalyst in 1 ml of ethanol solution, while the Pt/C catalyst (20 wt % Pt on Vulcan XC72R carbon) ink was prepared by dispersing 3 mg catalyst ultrasonically in a mixture solution containing in 1 mL ethanol solution. Every time, 10 μ L of catalyst ink were added with the 10 % of Nafion solution added milli Q water. The total amount of ink was dispersed on a glassy carbon rotating disk electrode (RDE) followed by drying at 60 °C. The catalyst loadings on RDE were 0.7 mg/cm² for hybrid catalysts and 85 μ g (Pt)/cm² for the Pt/C catalyst. A conventional three-electrode cell was employed incorporating a AgCl/Ag as the reference electrode, a Pt wire as the counter electrode and the catalyst film coated RDE as the working electrode. For oxygen reduction reaction (ORR), the RDE measurements were carried out at different rotation speeds between 600 and 2200 rpm in the O₂-saturated 0.1 M KOH aqueous solution. The RDE data were analysed using Koutecky-Levich (K-L) plots (J⁻¹ vs. $\omega^{-1/2}$) at different applied potentials. The slopes of the linear fit lines were used to calculate the electron transfer (ET) number (n) based on the Koutecky-Levich (K-L) equation:

$$1/J = 1/J_L + 1/J_k = 1/B\omega^{1/2} + 1/J_K$$

B= 0.62 n F C₀ (D₀)^{2/3}v^{-1/6}

Where,

- J= measured current density
- $J_k = Kinetic current$
- ω = electrode roation rate
- F= Faraday constant (96485 C/mol)

 C_0 = saturated concentration of O_2 in 0.1 M KOH solution at room temperature (1.2×10^{-6} mol/cm³)

 D_0 = Diffusion coefficient of O_2 in KOH (1.9 × 10⁻⁵ cm²/s)

v = kinetic viscosity of electrolyte (0.01 cm²/s)

According to the KL plot, the slope (1/B) can be used to calculate the ET number (n) namely,

 $n = B/0.62FC_0(D_0)^{2/3}v^{-1/6}$

To minimize the effect of the capacitive current, the linear sweep voltammetry (LSV) polarization curves recorded in O_2 -saturated 0.1M KOH solution have been normalized to the curves obtained after N_2 purging for 30 minutes. The CVs were recorded at a scan rate of 50 mV/s with rotation rate 600 rpm while the LSV curves were recorded at a scan rate of 10 mV/s at different rotation rates from 600 to 2200 rpm.

OER performance Test:

The LSV polarization curves were recorded in N₂ saturated 0.1 M KOH solution at different scan rate (10, 25, 50, 75 and 100 mV/s) at a rotation rate of 600 rpm. Tafel plots were recorded using the LSV which was performed at a sweep rate of 0.05 mV/s in the positive direction in a voltage range of 0 to 0.9 V vs. AgCl/Ag electrode. The stability test was performed by using LSV measurements at a scan rate of 100 mV/s.



Fig.2 (A and B) SEM images of commercial PB.

S1:

(a) 50 m

Fig. 3 SEM images of the product obtained by pyrolysing PB at 950 $^{\circ}$ C for 2 h. Both graphitic nanotubes and Fe-Fe₃C encapsulated N-graphene hybrid nanostructures were obtained.

When the pyrolysed temperature was raised babove 750 °C, N-doped graphitc nanotubes along with the encapsulated nanostructures were formed (Fig. 3). Fig. 4 (a and b) show the Fe-Fe₃C nanoparticles encapsulated graphitic structures. Fig. 4 (c and d) show the panoramic TEM images of graphitic nanotubes. It also shows that small Fe-Fe₃C nanoparticles were trapped inside the tubular structures. Fig. 4 (e and f) show the HRTEM images of edge portion of graphitic layers around Inanoparticles. The average diameter of the nanotubes was around 20-30 nm and the average length is 8-12

 μ m. Interestingly, the length of tube increases when the pyrolysis temperature was increased while the diameter iwas independent. Length of the tubes increases from ~4 to ~20 μ m from temperature range 850 to 1050 °C (**Fig.5**).



Fig.4 (a-d) TEM images of Fe-Fe₃C encapsulated nanostructures. (e and f) HRTEM images of encapsulated Fe-Fe₃C nanoparticles.



Fig.5 SEM images of N-doped CNT/graphene hybrid synthesized at different temperature region (a and b: 850 °C, c and d: 950 °C, e and f: 1050 °C, respectively).



Fig.5 (a and b) SEM images of the product obtained by pyrolysing PB at 1150 ^oC for 2 h. Ribbon like carbon nanostructures were formed.

When PB was pyrolyzed at high temperature, the tubular structure starts to degrade and ribbon like structures were formed.



Fig.6 HRTEM image of encapsulated nanostructures with few layer of graphitic layers.



Fig. 8 HRXPS spectra of encapsulated and hybrid nanostructures prepared at 750 and 850 °C.



Fig.9 EDS and elemental analysis of encapsulated nanostructures.



XPS spectra of N- doped hollow graphene nanostructures:



Fig. 10 (a) XPS survey spectra and (b) C 1s spectra of N-HG. (c) Fe 2p spectra for encapsulated nanostructures (black line) and N-HG (red line).

ORR activity of Pt/C catalyst:



Fig. 11 (a) Polarization curves of Pt/C with different rotation rate at 10 mV/s. (b) KL plot that yield the average number of electron transfer to be 3.92.

S4

850 °C synthesized N-doped graphene encapsulated Fe-Fe₃C hybrid:



S3:



Fig.12 (a) Polarization curves of hybrids synthesized at 850 0 C for 2h with different rotation rate at 10 mV/s. KL plot that yield the average number of electron transfer to be 3.82.



S5: ORR stability

Fig. 13 (a and b) CV of N-HG and 20% Pt/C in O₂-staurate 0.1M KOH solution. The black curve represents 1^{st} cycle, while the red curve represents 1000^{th} cycles. The scan rate was 50 mV/s and rotation speed was 600 rpm.

S6: % of N-doping dependent ORR



Fig. 14 CV of encapsulated nanostructures/hybrids synthesized at 750 and 850 $^{\circ}$ C. The scan rate is 50 mV/s and rotation speed is 600 rpm.

S7: Scan rate in dependent OER



Fig. 15 LSV curves of encapsulated nanostructures with different scan rate (10 to 100 mV/s) at a rotation speed of 600 rpm.

S8: N-doping dependent OER activity:



Fig. 16 LSV curves for encapsulated nanostructures/hybrids synthesized at 750 and 850 0 C. The scan rate was 50 mV/s and rotation speed was 600 rpm.

S-9:



Fig.17 LSV curves for encapsulated nanostructures/hybrids and hollow nanostructures and Pt/C. The scan rate is 10 mV/s and rotation speed was 1600 rpm.





Fig.18 stability curve for commercial RuO_2 representing 1st and after 1000th cycle (scan rate 100 mV/s and rotation speed of 600 rpm).



Fig.19 LSV curves encapsulated hydride nanostructures on the RDE (600 rpm) in 0.1M KOH (scan rate 50 mV/s), showing the electro-catalytic activities towards both ORR and OER on different potential range.

S-12:



Fig.20 XPS survey spectra of encapsulated hydride nanostructures after the 1000th cycles of stability of ORR (black line) and OER (red line) process.

S-11:

Table1: Comparison of the ORR catalytic activity of different hybrids.

Starting Materials (Cat. loading)	Catalyst	ORR Current density	Onset ORR potential	Medium	Reference
FeCl ₃ and cyanamide (NH ₂ CN) (0.43 mg/cm ²)	N-graphene/CNT hybrids	5.6 mA/cm ² at -0.25 V vs. Ag/AgCl	-0.08 V vs. Ag/AgCl (-0.03 V of 10 % Pt/C)	0.1 M KOH	Angew. Chem. Int. Ed. 2014, 53 , 6496 - 6500
Cyanamide and FeCl ₃	N-Fe/Fe ₃ C@C	0.91 V (at 0.1 V vs. Ag/AgCl) (Compared with 10 % Pt/C)		phosphate buffer solution (0.1 M PBS, pH = 7.0)	<i>Adv. Mater.</i> 2012, 24 , 1399-1404
Pluronic P123 (P123), melamine and Fe(NO ₃) ₃ (1.2 mg/cm^2) Cat and 25 µg _{Pl} /cm ²)	Bamboo-like Carbon Nanotube/Fe ₃ C Nanoparticle	Comparable half wave potential	0.886 V Cat. 0.93 V Pt/C (vs. RHE)	0.1 M KOH	J. Am. Chem. Soc. 2015, 137 , 1436- 1439
Ferrocene and Cyanamide (0.6 mg/cm ² catalyst compared with 0.25 mg/cm ² Pt/C 50 μg _{Pt} /cm ²)	Hollow Spheres of Iron Carbide Nanoparticles Encased in Graphitic Layers	Comparable current density and onset potential with Pt/C		0.1 M HClO ₄	Angew. Chem. Int. Ed. 2014, 53 , 3675- 3679
N,N- Dimethylformamide (DMF), FeCl ₃ ·6H ₂ O, and terephthalic acid (0.1 mg/cm ²)	N-doped Fe/Fe ₃ C@ graphitic layer/carbon nanotube	Low current values compared with 20 % Pt/C	0.04 V vs Ag/AgCl (0.045V vs. AgCl/Ag)	0.1 M KOH	<i>Chem. Commun.</i> , 2015, 51 , 2710-2713
Prussian blue (Iron (III) ferrocyanide (Fe ^{III} ₄ [Fe ^{II} (CN) ₆] ₃	N-doped Fe-Fe ₃ C@ graphitic layer	3.7 mA/cm ² (at 0.25 V vs. Ag/AgCl)	-0.05 V vs. Ag/AgCl	0. 1 M KOH	This work
(0.71 mg/cm ² both the catalyst and 0.428 mg/cm ² of 20 % Pt/C)	N-doped hollow graphitic structures	4.8 mA/cm ² (at 0.25 V vs. Ag/AgCl)	at -0.05 V vs. Ag/AgCl (20 % Pt/C: -0.03 V vs. Ag/AgCl)		

Table2: Comparison of the OER catalytic activity and onset potentials of different Catalyst

Catalyst	OER Potential at 10 mA/cm ²	Loading	Medium	Ref.
N-graphene/CNT hybrids	1.65 V vs. RHE	0.43 mg/cm ²	0.1 M KOH	Angew. Chem. Int. Ed. 2014, 53 , 6496 -6500
Nitrogen-doped Fe/Fe ₃ C@ graphitic layer/carbon nanotube	~1.1 V vs. AgCl/Ag	0.1 mg/cm ²	0.1 M KOH	<i>Chem. Commun.</i> , 2015, 51 , 2710-2713
Commercial RuO ₂	0.78 V vs. AgCl/Ag	0.215 mg/cm ²	0.1 M KOH	This work
Nitrogen-doped Fe/Fe ₃ C@ graphitic layer	0.778 V vs. AgCl/Ag	0.71 mg/cm ² both the catalyst	0. 1 M KOH	This work
N-doped hollow graphitic structures	0.77 V vs. AgCl/Ag			

Table3: Comparison of the ORR catalytic activity and onset potentials of 20% of Pt/C catalyst

Catalyst	Current density (mA/cm ²)	Onset potential	Loading	Medium	Ref.
10 % Pt/C	~ 2.8 mA/cm ² at -0.25 V at AgCl/Ag	-0.03 V vs. AgCl/Ag	$0.43 \ \mu g_{Pt}/cm^2$	0.1 M KOH	Angew. Chem. Int. Ed. 2014, 53 , 6496 -6500
20 % Pt/C	4.6 mA/cm ² at -0.25 V at AgCl/Ag	-0.03 V vs. AgCl/Ag	0.85 µg _{Pt} /cm ²		This work

Conversion factor from Ag/AgCl electrode to RHE : AgCl/Ag + 0.967 V

(RHE = Ag/AgCl (Sat. KCl) + 0.197 V + 0.0591 pH at 25 °C).