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Supplementary Information

Fe-based non-noble metal catalysts with dual active sites of nanosized metal carbide and single-atomic species for oxygen reduction reaction

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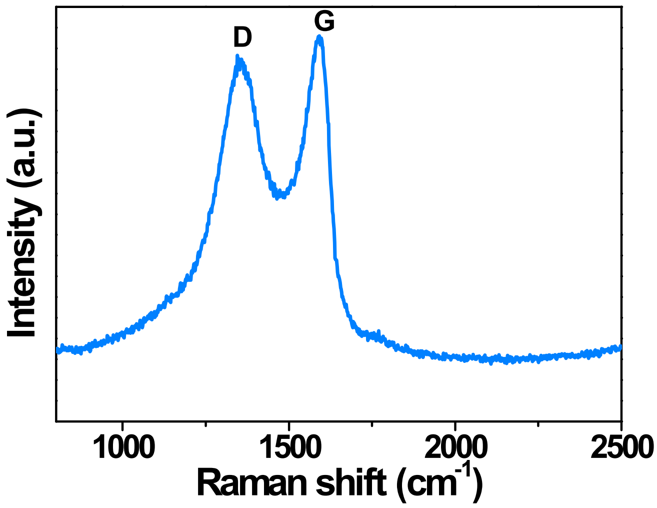

Fig. S1. Raman spectrum of graphene oxide.

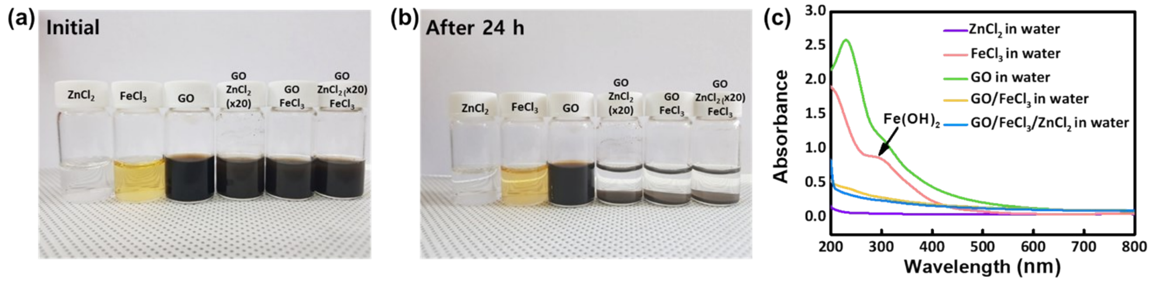

Fig. S2. (a-b) Photographs of the dispersibility test and (c) absorption spectra of the supernatants of the mixtures.

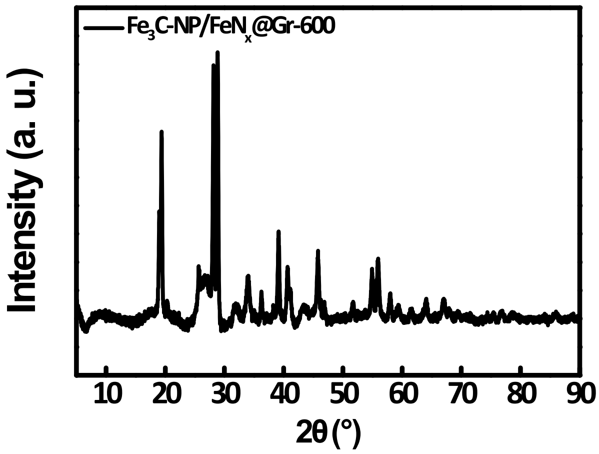

Fig. S3. XRD diffractogram of Fe_3C-NP/FeN_x@Gr-600.

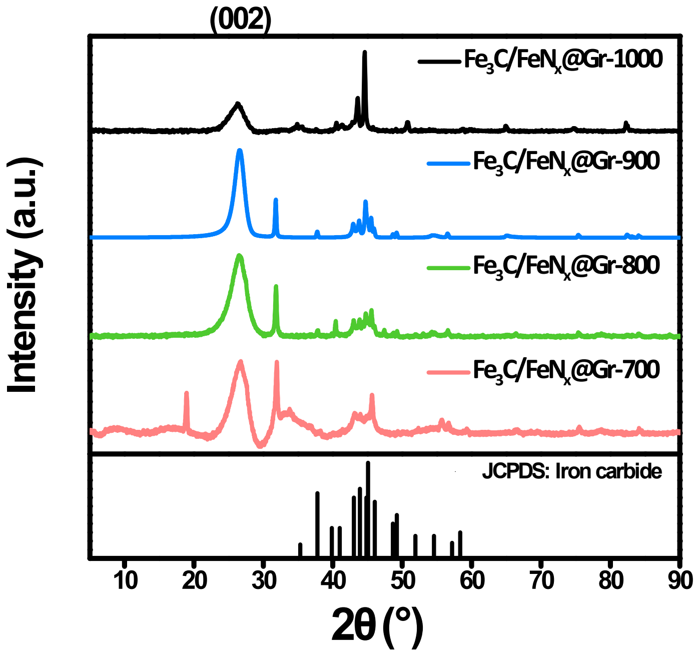

Fig. S4. XRD of Fe_3C/FeN_x@Gr samples prepared at different pyrolysis temperatures.

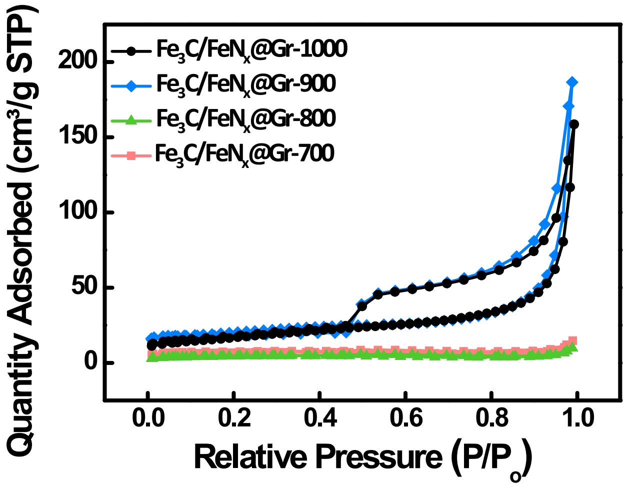

Fig. S5. Isotherms of Fe_3C/FeN_x@Gr samples prepared at different pyrolysis temperatures.

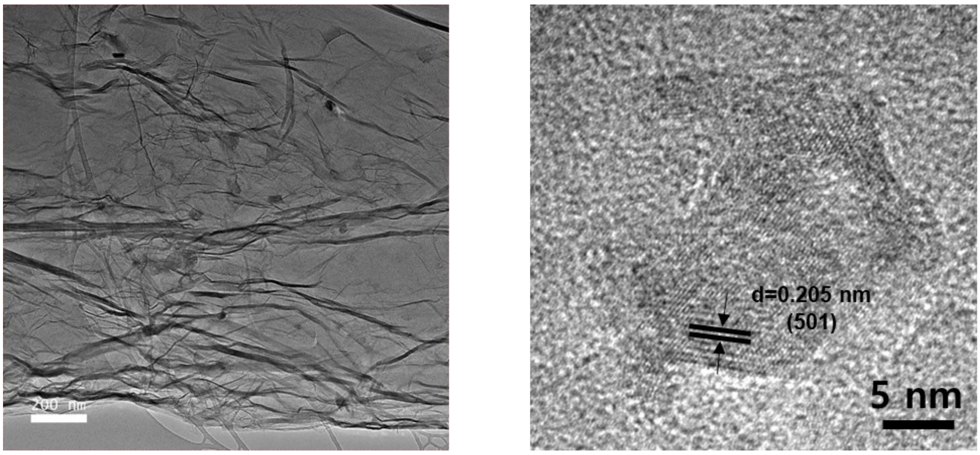

Fig. S6. TEM images of Fe_3C/FeN_x@Gr-900.

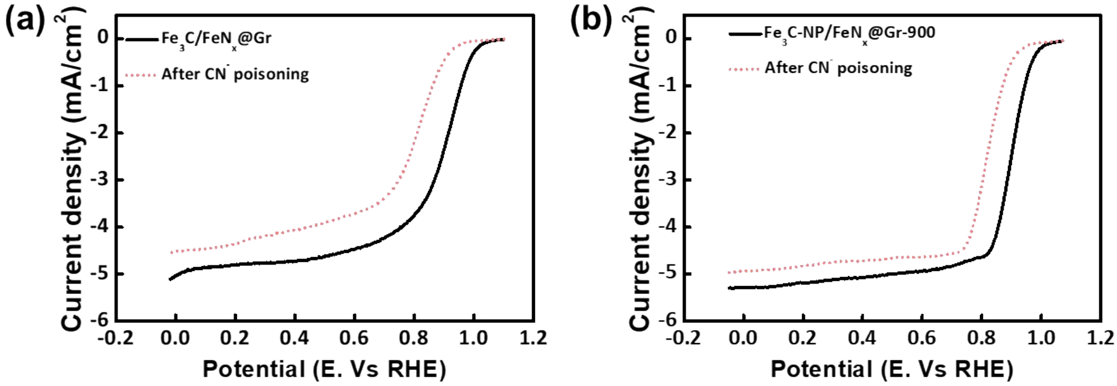

Fig. S7. ORR polarization curves of (a) Fe_3C/FeN_x@Gr-900 and (b) Fe_3C-NP/FeN_x@Gr-900 with the addition of 0.01 M NaCN.

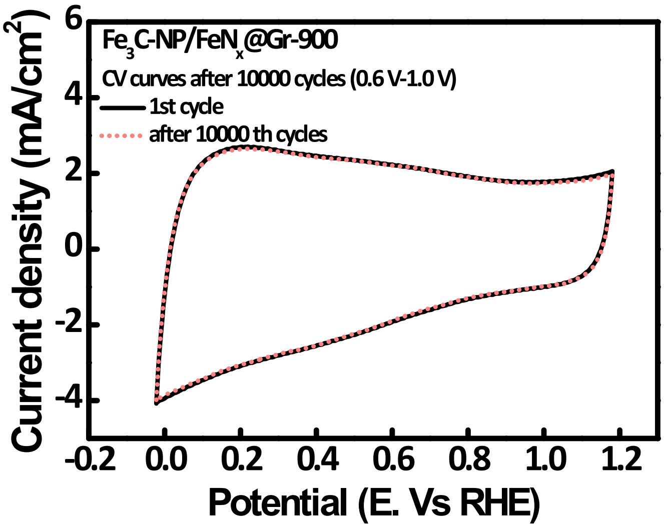

Fig. S8. Cyclic voltammogram of Fe_3C-NP/FeN_x-900 before and after 10,000 cycles.

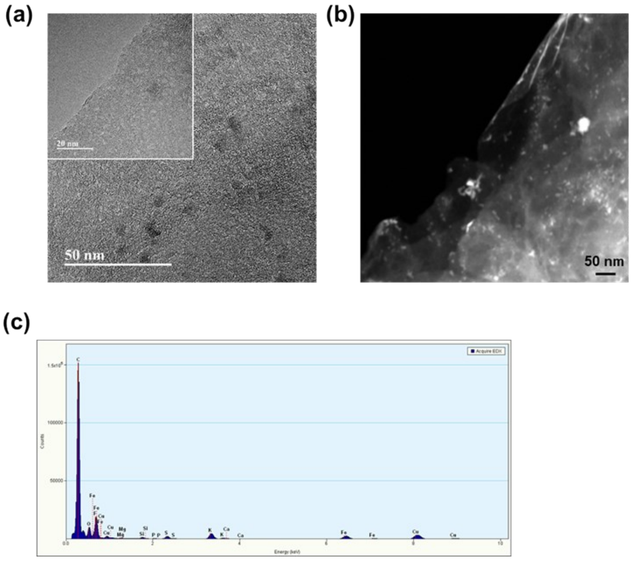

Fig. S9. (a) HR-TEM, (b) HAADF-STEM images and (c) corresponding EDX spectra of the Fe_3C-NP/FeN_x-900 catalyst after 10,000 cycles.

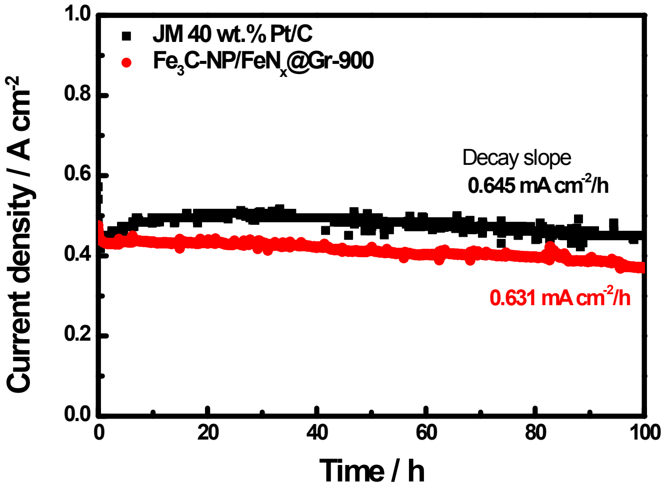

Fig. S10. Alkaline membrane fuel cell performance durability tests at a constant voltage of 0.6 V for the MEAs with Fe_3C-NP/FeN_x@Gr-900 and Pt/C as cathode catalysts.

Table S1. (a) K_a values of hydrated Zn and Fe species, (b) pH values of $ZnCl_2$ and $FeCl_3$ in deionized water

(a)

Free Ion	**Hydrated Ion**	K_a
Zn^{2+}	$Zn(H_2O)_6^{2+}$(aq.)	1×10^{-9}
Fe^{3+}	Fe(H2O)$_6^{3+}$(aq.)	6×10^{-3}

- Reaction in water

$FeCl_3 + H_2O \rightarrow Fe(H_2O)_6^{3+} + 3Cl^-$

$Fe(H_2O)_6^{3+} \rightarrow Fe(H_2O)_5(OH)^{2+} + H_3O^+$

(b)

Sample	**pH**
$ZnCl_2$	5.86
$FeCl_3$	2.84
H_2O	6.77

Fe^{3+} is more acidic than Zn^{2+}, because the K_a value of Fe^{3+} is higher than that of Zn^{2+}.

Therefore, Fe^{3+} ions can more strongly bind to the surface of negatively charged graphene oxide than Zn^{2+} ions.

Table S2. Atomic contents of (a) Fe_3C/FeN_x@Gr and (b) Fe_3C-NP/FeN_x@Gr samples

(a)

	C (at.%)	N (at.%)	O (at.%)	Fe (at.%)	Zn (at.%)
Fe_3C/FeN_x@Gr-700	70.9	9.2	19.1	0.8	-
Fe_3C/FeN_x@Gr-800	77.5	10.3	11.8	0.4	-
Fe_3C/FeN_x@Gr-900	81.6	8.7	9.3	0.4	-
Fe_3C/FeN_x@Gr-1000	94.6	1.9	3.1	0.4	-

(b)

	C (at.%)	N (at.%)	O (at.%)	Fe (at.%)	Zn (at.%)
Fe_3C-NP/FeN_x@Gr-700	76.5	11.9	10	0.4	1.2
Fe_3C-NP/FeN_x@Gr-800	84.2	7.7	7.4	0.5	0.2
Fe_3C-NP/FeN_x@Gr-900	84.8	7.9	6.7	0.5	0.1
Fe_3C-NP/FeN_x@Gr-1000	96	1.5	2.1	0.4	0

Table S3. BET surface area (SA) (micropore SA and external SA) and pore volume of (a) Fe_3C/FeN_x@Gr and (b) Fe_3C-NP/FeN_x@Gr samples

(a)

	Fe_3C/FeN_x@Gr-700	**Fe_3C/FeN_x@Gr-800**	**Fe_3C/FeN_x@Gr-900**	**Fe_3C/FeN_x@Gr-1000**
BET area (m^2/g)	19.9	15	68.4	59.7
Micro SA (m^2/g)	9.5	6	21.7	1
External SA (m^2/g)	10.4	9	46.7	58.7
Pore volume at 0.9 P/Po (m^3/g)	0.022	0.015	0.289	0.246

(b)

	Fe_3C-NP/FeN_x@Gr-700	**Fe_3C-NP/FeN_x@Gr-800**	**Fe_3C-NP/FeN_x@Gr-900**	**Fe_3C-NP/FeN_x@Gr-1000**
BET SA (m^2/g)	20.7	11.7	235.3	374.8
Micro SA (m^2/g)	5.8	-	24.8	11.7
External SA (m^2/g)	14.9	11.7	210.5	363.1
Pore volume at 0.9 P/Po (m^3/g)	0.031	0.016	1.21	1.68

Table S4. Comparison of the AEMFC performances of Fe-based catalysts

Catalyst	P_{max} (mW cm^{-2})	J_{max} (mA cm^{-2})	Cathode loading (mg cm^{-2})	Iron contents	Ref.
Our catalyst	**367**	**1043**	**3.0**	**5.2 wt.% (ICP-AAS)**	
Fe carbide+Fe-N_x catalyst	243	~680	2.0	2.0 wt.% (ICP-MS)	52
Fe_3C/Fe-N_x	160	~420	2.0	1.5 at.% (XPS)	51
Fe/Fe_3C	96	~400	2.0	13.88 wt.% (SEM-EDX)	53
Fe-N, Fe_3C, Fe_2O_3	50	~280	2.0	41.26 mg L^{-1} (ICP-AES)	54
Fe_3C	125	~460	3.0	1.48 at.% (XPS)	55
Fe-N_x/CNT	635	~2100	1.5	0.8 wt.% (ICP-OES)	30
Fe-N_x	140	~660	3.5	0.22 at.% (XPS)	56
FeN_x/FeS_x	65	~250	2.0	1.15 wt.%	57

				(EDAX)	
Fe/Co-N	35	~110	2.5	3.8 wt.% (Fe), 3.6 wt% (Co) (EDAX)	58
Fe-Fe_2O_3	54	~200	3.0	48.69 wt.% (XPS)	59