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Supplementary Information

Self-templated synthesis of novel and robust honeycomb-like N-doped highly graphitized carbon from low-temperature carbonization

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Experimental Section

1. Materials

Urea ($CO(NH_2)_2$), hydrochloric acid (HCl, 35.0-37.0%), cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$), ethanol (CH_3CH_2OH, 99.9%), 2-propanol ($(CH_3)_2CHOH$, 99.9%) and ethylene glycol ($(CH_2OH)_2$, EG, 99.5%) were provided by Samchun Pure Chemicals. Mg powder, chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$), and Nafion solution (5wt%) were purchased from Sigma-Aldrich.

2. Synthesis of honeycomb-like N-doped graphitic carbon (HNGC-X)

Graphitic carbon nitride (g-C_3N_4) was prepared from the polymerization of urea.[1] Briefly, 30 g of urea was transferred to an alumina crucible with a cover and heated at 550 ℃ for 4 h under an air atmosphere in a muffle furnace. 2 g of as-prepared g-C_3N_4 was mixed with 2 g of Mg powder.[2-4] The well-mixed composite was held in a covered alumina crucible and heated at 750~950 ℃ for 5 h with a heating rate of 3 ℃ min^{-1} under an inert atmosphere (N_2 or Ar flow) in the tube furnace. The product was collected and stirred in 2.0 M HCl solution for 5 h and filtered, followed by thorough washing with distilled water before drying at 60 ℃ for 12 h. The final product was denoted as HNGC-X, where X stands for the carbonization temperature. In addition, control HNGC-750 samples were prepared from 2 g of g-C_3N_4 with 0.5, 1.0, and 4.0 g of Mg and denoted as HNGC-750-YMg, where Y represents the grams of Mg used.

3. Pt_1Co_1 deposition on HNGC-X using a microwave reactor

PtCo nanoparticles (NPs) deposition was carried out by a modified homogeneous deposition method[5] with the microwave reactor. 80 mg of HNGC-X was dispersed in 300 mL of EG-distilled water solution (9:1 vol.) with 310 mg of urea. After sonication for 20 min, 156 μL of 0.5 M $CoCl_2 \cdot 6H_2O$ solution and 156 μL of 0.5 M $H_2PtCl_6 \cdot 6H_2O$ solution were added and stirred for 3 h. Then, the homogeneous solution was transferred to a Teflon vessel and heated up through two steps of 90 ℃ for 10 min and 120 ℃ for 5 min, using a microwave reactor (Masterwave BTR, Anton Paar). The sample was filtered and washed with ethanol and distilled water several times. The loading amount for all Pt/HNGC-X was 20 wt% as confirmed by the TGA results. For comparison, PtCo was also loaded on the commercial carbon support; Vulcan XC 72R (VC), through the same process with Pt/HNGC-X.

4. Characterization

The scanning electron microscopy (SEM) images were collected using a Hitachi S-4700 microscope operated at an acceleration voltage of 10 kV. The transmission electron microscopy (TEM) images were obtained using an FEI/Tecnai G2 F20 TWIN TMP microscope, operated at 200 kV. HNGC-750 before and after etching embedded in epoxy resin were sectioned using an ultra-microtome (Lecia EM UC7) and the slices with a thickness of ~20 nm were allocated to copper grids for TEM images. N_2 adsorption-desorption isotherms were obtained at -196 ℃ using a Micromeritics ASAP 2460 surface area and porosity analyzer after the samples were degassed at 150 ℃ to 20 mTorr for 12 h. The specific surface area was determined based on the Brunauer-Emmett–Teller (BET) method from N_2 adsorption data in the relative pressure range from 0.05 to 0.2. Powder X-ray diffraction (XRD) patterns of the samples were recorded using a Rigaku Smartlab diffractometer with Cu-Kα (λ=0.15406 nm) operated at 15 mA and 40 kV with a scan rate of 4° min^{-1}. Raman spectra were recorded by a NICOLET ALMECA XR spectrometer with 532 nm laser beam used for excitation. X-ray photoelectron spectroscopy (XPS) was carried out using an ESCALAB 250 XPS System with a monochromated Al Kα (150 W) source. The energy scale is aligned by using the Fermi level of the XPS instrument (4.10 eV versus absolute vacuum value). The thermogravimetric analysis (TGA) was performed to confirm the metal loading amount in HNGC-X using a Bruker TGDTA2000SA analyzer. The atomic ratio of Pt and Co was analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES) using an iCAP7400 (Thermo Scientific). For the ICP-OES measurement, 10 mg of each sample was added to 10 mL of aqua regia. After a day, Pt and Co dissolved solution was diluted 20 times with DI water before the ICP analysis.

5. Electrochemical measurements

Electrochemical measurements for the oxygen reduction reaction (ORR) were conducted with a three-electrode system at room temperature using a rotating disk electrode (RDE) connected to an electrochemical analyzer (Biologic VMP3), including Ag/AgCl with saturated KCl and a Pt wire as a reference and counter electrode, respectively. The Ag/AgCl reference electrode was calibrated in terms of RHE. The working electrode was a glassy carbon (GC) electrode with a 3 mm diameter coated with either PtCo/HNGC-X, PtCo/VC, or commercial Pt/C (20% Pt on Ketjen black, Tanaka). The catalyst ink was prepared by dispersing 5.0 mg of catalysts

in a mixture of 0.1 ml 5 % Nafion solution (Sigma Aldrich) and 0.9 ml DI water. The dispersed ink was cast over GC electrode and dried at 60℃ in an oven. The metal (PtCo) loading on the electrode was about 5 μg cm^{-2}. The cyclic voltammetry (CV) experiments were performed in N_2-saturated 0.1 M HClO4 solution with a scan rate of 50 mV s^{-1} in the potential range from 1.1 to 0.05 V. RDE measurements were also performed for ORR by recording linear sweep voltammetry (LSV) curves in 0.1 M $HClO_4$ solution. The LSV curves at 1600 rpm were recorded between +1.0 and -0.2 V at a potential scan rate of 10 mV s^{-1}, where the Pt ring potential was measured at a set potential of +1.1 V. The LSV curve from O_2-purged 0.1 M $HClO_4$ solution was normalized by the LSV result in the N_2-saturated 0.1 M $HClO_4$ solution.

Membrane electrode assemblies (MEAs) were prepared using the catalyst-coated membrane (CCM) with an active area of 5 cm^2. As-synthesized PtCo/HNGC-750 or PtCo/VC was used as an active cathode electrode, while the commercial Pt/C (20 wt% Pt on Ketjen black, Tanaka) was used as an anode catalyst. All the catalysts inks were composed of 15 mg of catalyst powder, 100 mg of 2-propanol, 120 mg of DI water, and 100 mg of 5 wt% Nafion solution. The well-dispersed catalyst slurry was directly sprayed onto a Nafion N211 membrane using an air spray gun. The loading amount was 0.1 mg_{metal} cm^{-2} and the prepared CCMs were dried at 60 ℃ for 6 h. The MEAs were assembled with commercial gas diffusion layers (GDL, SGL 39BB) without hot-pressing. PEMFC performance was measured at 80 ℃ with a back pressure of 0.5 bar where fully humidified H_2 and O_2 (or Air) were supplied to the anode and cathode at a flow rate of 300 and 1000 mL min^{-1}, respectively. The polarization curves for MEAs were obtained under constant current mode using an electronic load (PLZ664WA, Kikusui) with a PEMFC test station (Scitech Inc., Korea).

To test the durability of carbon support, an accelerated durability test (ADT) was carried out according to catalyst support cycles from the Department of Energy (DOE).[6] The 5k cycles were performed between 1.0 V and 1.5 V with a scan rate of 500 mV s^{-1} under fully humidified H_2/N_2 flow at 80 ℃ in ambient pressure. The polarization curves, CVs, and EIS were obtained before and after 5k cycles. The electrochemical active surface area (ECSA) was calculated by following equation;

$$ECSA\left(m^2/g\right) = \frac{Q_H\ (uC/cm^2)}{[Pt]\ \left(g/m^2\right) \times 210_{uC/cm^2}}$$

where [Pt] is Pt loading amount on electrode, 210 uC cm^{-2} is the charge required to oxidize a monolayer of hydrogen on Pt theoretically, and QH is total charge of hydrogen desorption which is calculated from CV.[7]

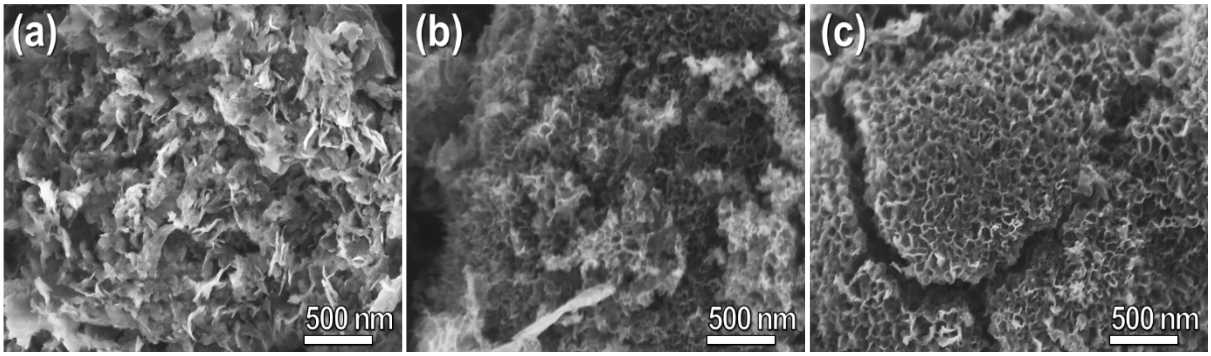

Fig. S1 SEM images for (a) g-C_3N_4, (b) HNGC-850, and (c) HNGC-950.

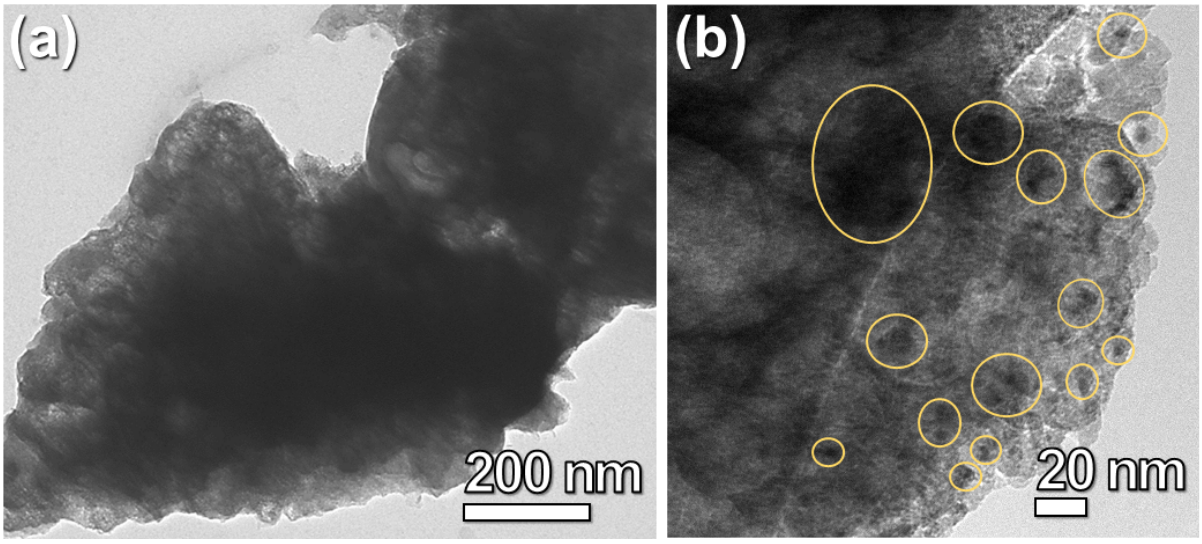

Fig. S2 (a and b) TEM images for HNGC-750-BE in different magnifications. Yellow circles in Fig. S2b indicate the Mg_3N_2 particles embedded in the carbon matrix.

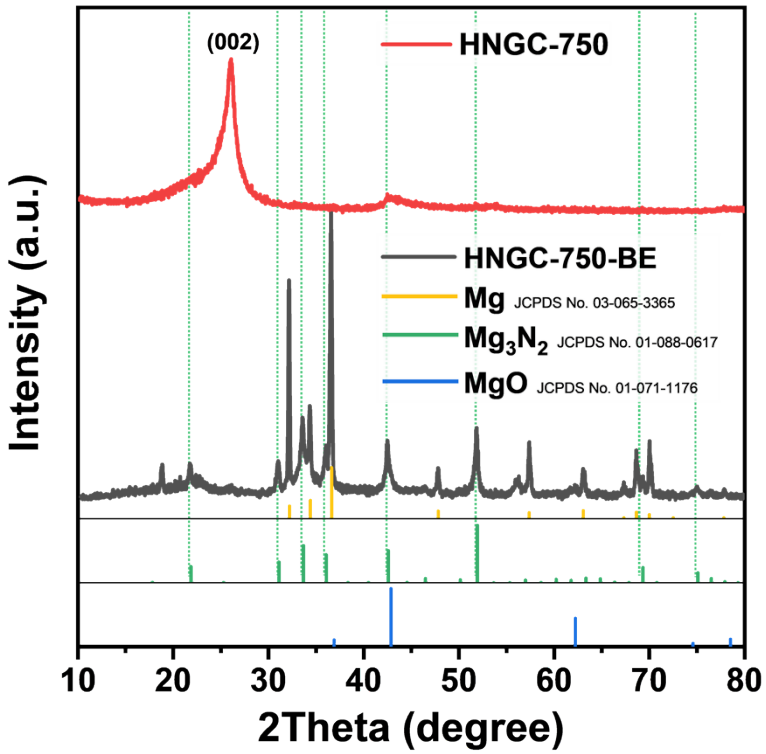

Fig. S3 XRD patterns of HNGC-750-BE (bottom) showing the presence of in-situ generated Mg_3N_2 and HNGC-750 (top).

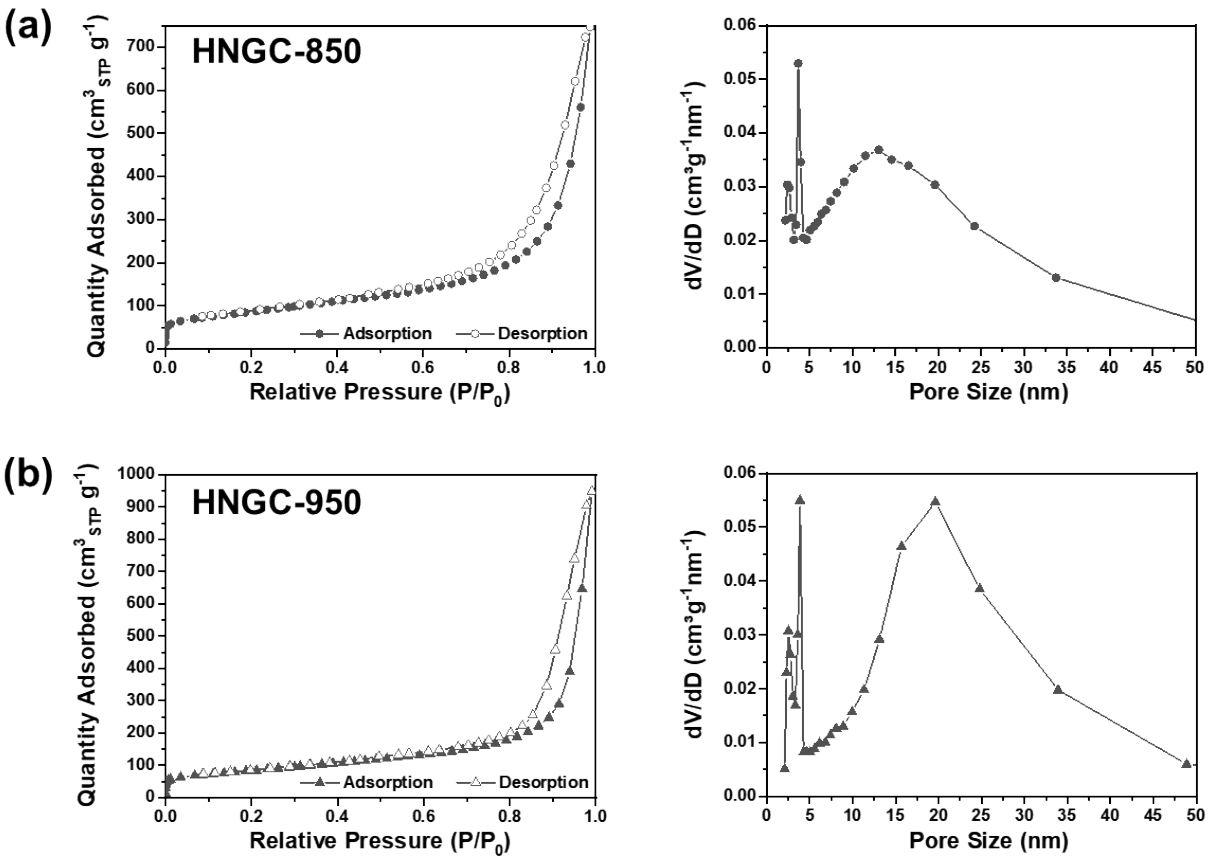

Fig. S4 N_2 gas adsorption-desorption curves and the corresponding pore size distribution of (a) HNGC-850 and (b) HNGC-950.

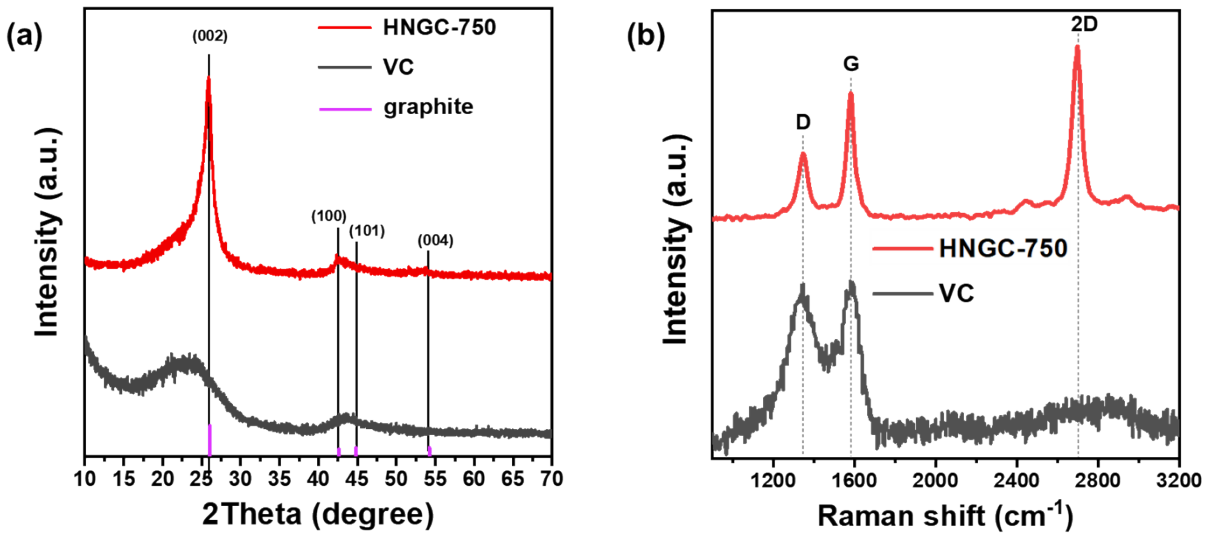

Fig. S5 (a) XRD patterns and (b) Raman spectra of HNGC-750 and VC.

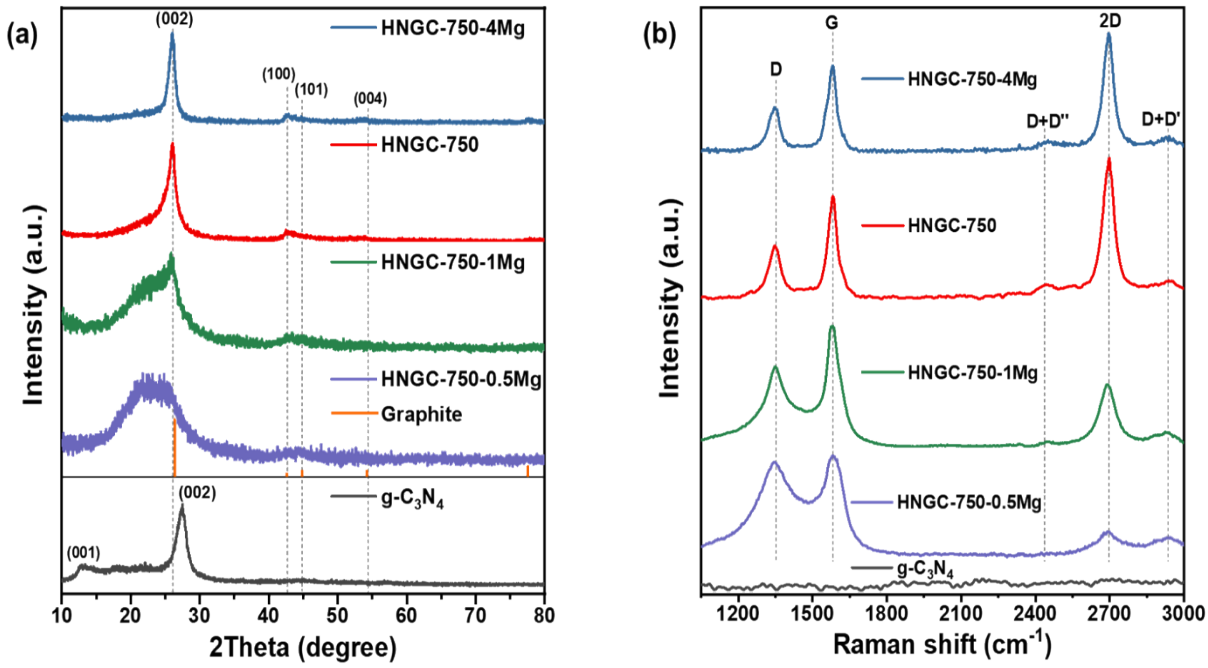

Fig. S6 (a) XRD patterns and (b) Raman spectroscopy data from the HNGC-750 samples prepared with identical synthesis conditions except varying the amount of Mg (HNGC-750-YMg). Note that the HNGC-750 was prepared by 2 g Mg.

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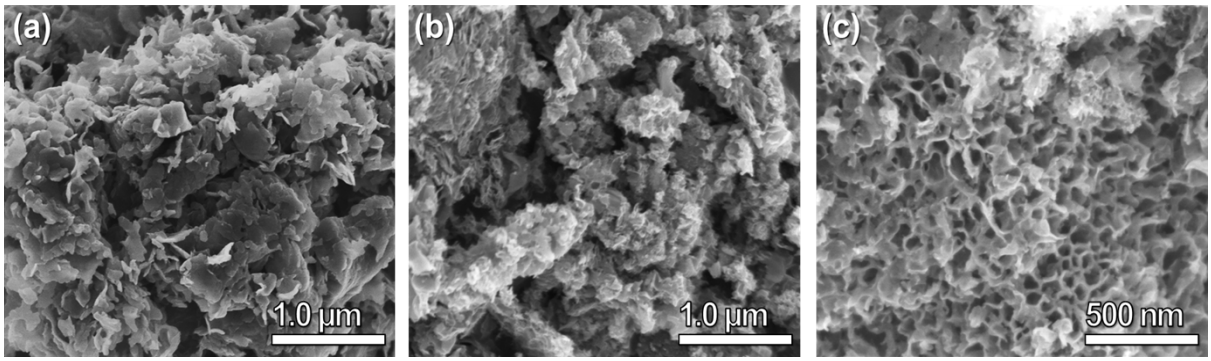

Fig. S7 SEM images for (a) HNGC-750-0.5Mg, (b) HNGC-750-1Mg, and (c) HNGC-750-4Mg.

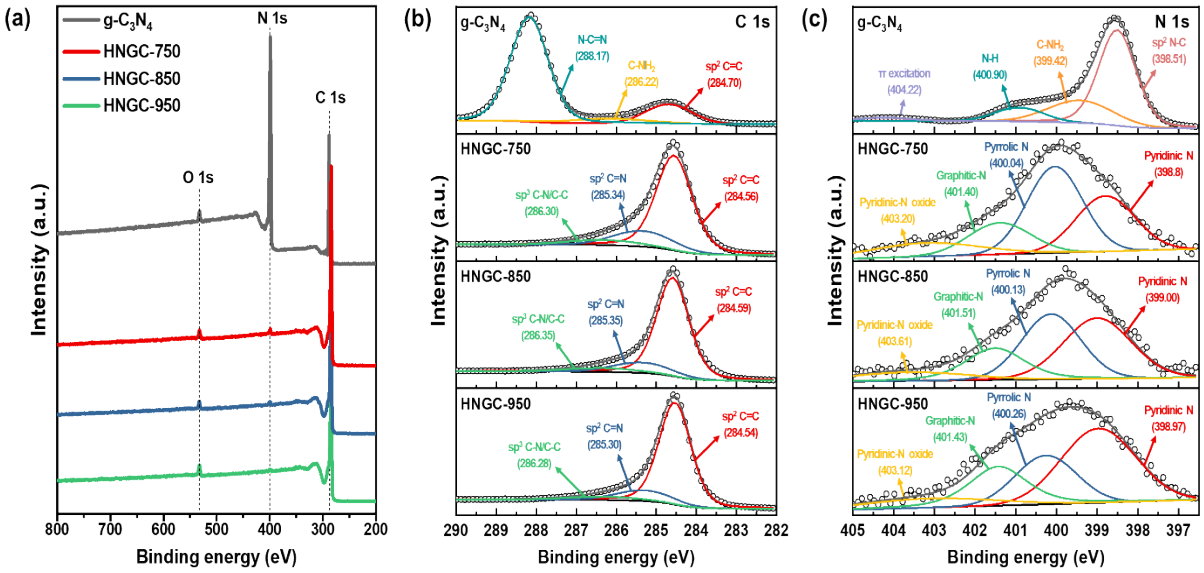

Fig. S8 (a) XPS survey spectra for g-C_3N_4, HNGC-750, 850, and 950 and the corresponding high-resolution XPS profiles for (b) C 1s and (c) N 1s.

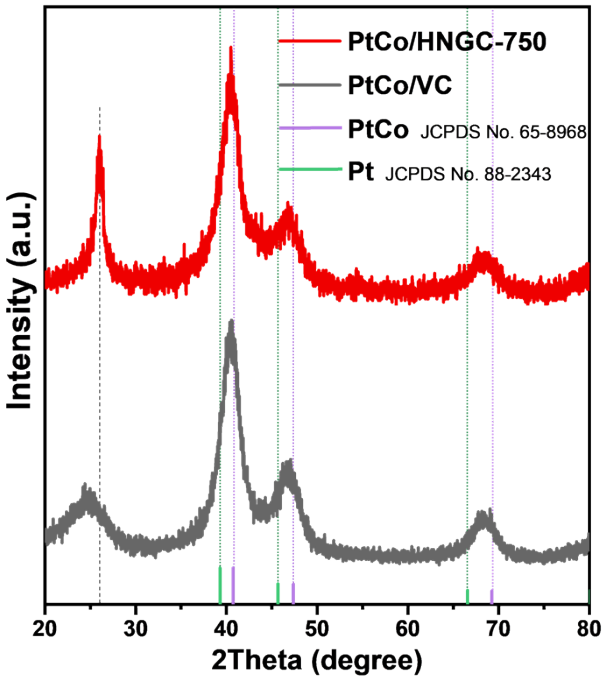

Fig. S9 XRD patterns for PtCo/VC and PtCo/HNGC-750

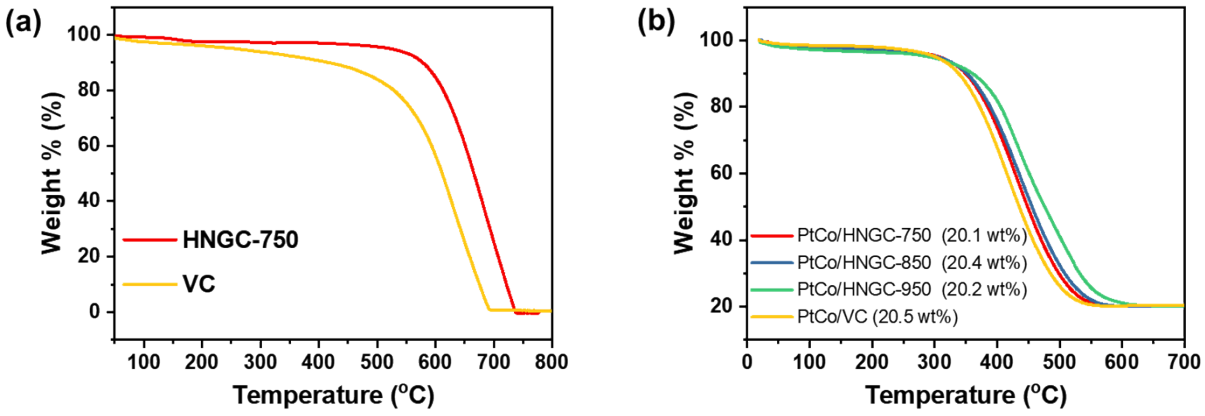

Fig. S10 TGA profiles of the as-prepared samples measured under air condition.

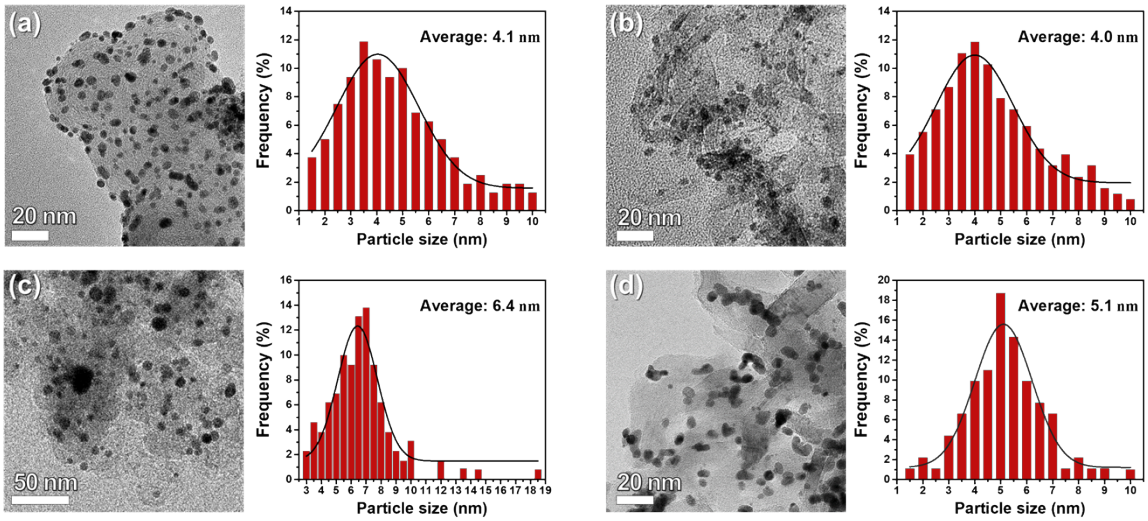

Fig. S11 TEM images and corresponding Pt particle size distribution histograms (a, b) before and (c, d) after accelerated durability test (ADT) for catalyst support durability of PtCo/VC and PtCo/HNGC-750, respectively.

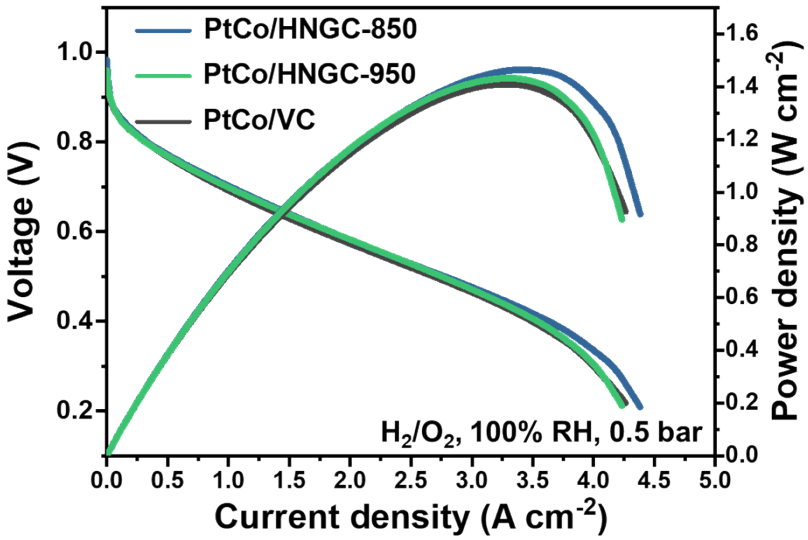

Fig. S12 Single cell polarization and power density curves for PtCo/HNGC-850, PtCo/HNGC-950, and PtCo/VC in fully humidified H_2/O_2. The polarization curves of the MEAs were obtained by using a cathode catalyst loading of 0.1 g_{PtCo} cm^{-2} at 80 °C under a backpressure of 0.5 bar.

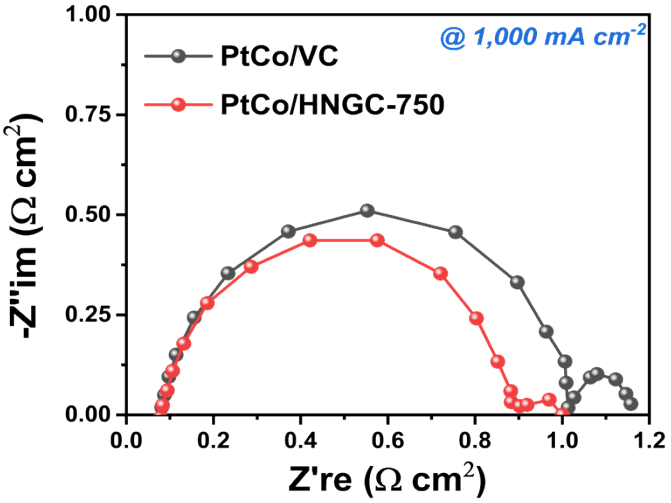

Fig. S13 Electrochemical impedance spectroscopy (EIS) profiles for PtCo/VC and PtCo/HNGC-750 at 1.0 A cm $^{-2}$. EIS of MEAs were tested at 80 °C with fully humidified H_2/Air and backpressure as 0.5 bar.

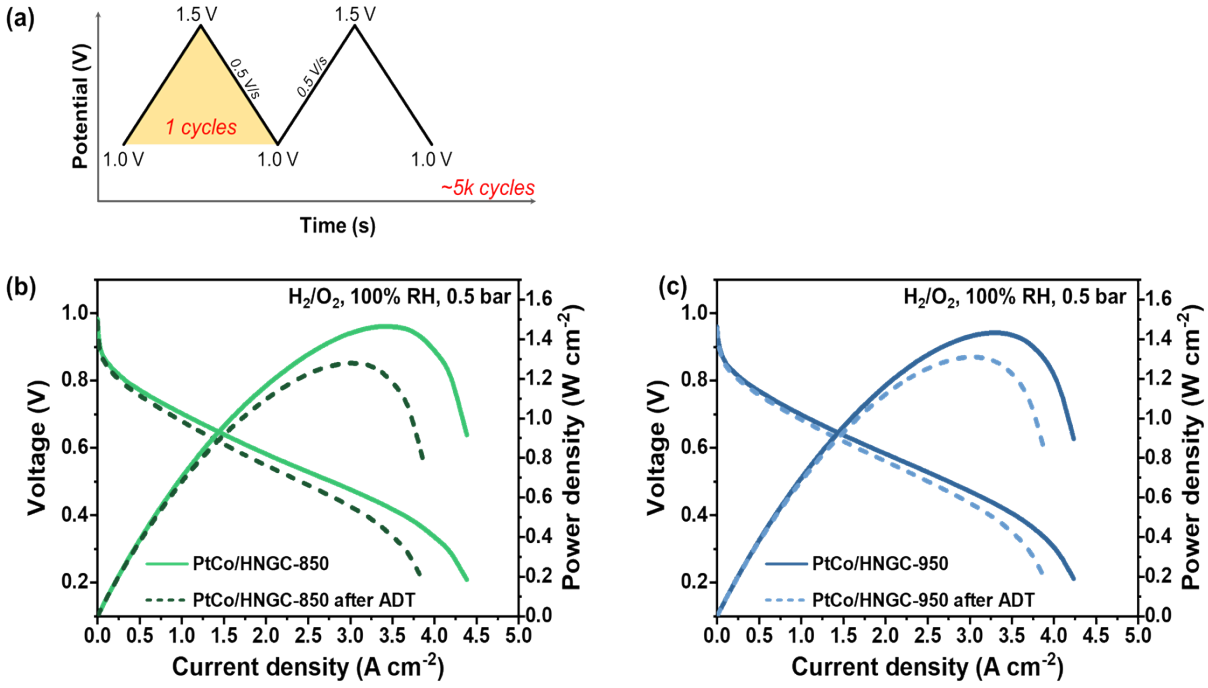

Fig. S14 (a) DOE 5k cycle accelerated durability test (ADT) protocol for carbon support degradation.[6] Single cell polarization and power density curves for (b) PtCo/HNGC-850 and (c) PtCo/HNGC-950 before and after carbon support ADT. The polarization curves of the MEAs were obtained by using a cathode catalyst loading of 0.1 g_{PtCo} cm^{-2} at 80 °C under a backpressure of 0.5 bar with fully humidified H_2/O_2.

Table S1 BET surface area, pore volume, and average pore diameter for the as-prepared samples and Vulcan XC 72R (VC).

Sample	BET surface area ($m^2 g^{-1}$)	Total pore volume ($cm^3 g^{-1}$)	Micropore volume ($cm^3 g^{-1}$)	Mesopore volume ($cm^3 g^{-1}$)	Average pore diameter (nm)
g-C_3N_4	81 ± 2.4	0.47	0.009	0.46	23.3
HNGC-750	320 ± 9.6	1.13	0.007	1.12	12.3
HNGC-850	305 ± 9.2	1.20	0.005	1.19	13.9
HNGC-950	296 ± 8.9	1.51	0.002	1.51	18.0
HNGC-750-0.5Mg	434 ± 13.0	0.91	0.028	0.88	7.9
HNGC-750-1Mg	398 ± 11.9	0.98	0.016	0.96	9.6
HNGC-750-4Mg	302 ± 9.1	1.29	0.007	1.28	14.8
Vulcan XC 72R (VC)	212 ± 6.4	0.47	0.042	0.43	16.1

Table S2 I_D/I_G and I_{2D}/I_G calculated from Raman spectra of HNGC-X.

Sample	$\frac{I_D}{I_G}$	$\frac{I_{2D}}{I_G}$	FWHM of 2D peak (cm^{-1})[6]
HNGC-750	0.52	1.21	57 (~3 layers)
HNGC-850	0.27	1.48	50 (~2 layers)
HNGC-950	0.21	1.54	48 (~2 layers)
HNGC-750-0.5Mg	0.90	0.24	136 (multi layers)
HNGC-750-1Mg	0.63	0.56	72 (multi layers)
HNGC-750-4Mg	0.50	1.31	54 (~ 2 layers)
Vulcan XC 72R (VC)	1.00	-	-

Table S3 Atomic percentage of C, N, O, and Cl determined from the XPS survey scans of different samples in Fig. S8a.

Sample	C 1s (at%)	N 1s (at%)	O 1s (at%)	Cl 2p (at%)*
g-C_3N_4	47.3	51.5	1.2	0
HNGC-75	95.2	2.1	2.5	0.2
HNGC-85	96.1	1.3	2.3	0.2
HNGC-95	96.3	0.8	2.8	0.1
HNGC-750-0.5Mg	93.0	2.8	4.1	0.1
HNGC-750-1Mg	93.6	2.4	3.8	0.2
HNGC-750-4Mg	95.7	1.8	2.4	0.1
Vulcan XC 72R (VC)	96.3	0	3.7	0

* Cl contents were from HCl etching.

Table S4 Atomic percentage of N species in the as-prepared samples calculated from the high-resolution N 1s XPS spectra in Fig. S8c.

Sample	Total N (at%)	sp^2 N-C (at%)	C-NH_2 (at%)	N-H	Pyridinic-N (%)	Pyrrolic-N (%)	Graphitic-N (%)	Pyridinic-N oxide (%)
g-C_3N_4	51.5	64.6	24.1	11.3	0	0	0	0
HNGC-75	2.1	0	0	0	28.4	41.6	17.1	12.9
HNGC-85	1.3	0	0	0	37.5	34.2	19.4	8.9
HNGC-95	0.8	0	0	0	44.1	23.9	22.3	9.7

Table S5 Atomic and weight ratio of PtCo alloy deposited on VC and HNGC-X by ICP-OES.

Sample	Atomic ratio Pt:Co	Weight ratio* Pt:Co
PtCo/HNGC-75	54:46	79:21
PtCo/HNGC-85	55:45	80:20
PtCo/HNGC-95	57:43	81:19
PtCo/VC	55:45	80:20

* Weight ratio was calculated from atomic composition.

Table S6 Summary of the MEA results from commercial 20% Pt/C, PtCo/VC, and PtCo/HNGC-X before and after 5k cycle accelerated durability test (ADT) for carbon support tested under H_2/O_2.

Catalyst	Cycle number	P_{max} (W cm^{-2})	Mass activity* (A mg_{Pt}^{-1})	V @ 0.8 A cm^{-2} (V)	V @ 1.5 A cm^{-2} (V)
Commercial 20% Pt/C	Initial	1.35	0.22	0.704	0.619
PtCo/VC	Initial	1.41	0.39	0.719	0.628
	After 5k	0.60	0.18	0.557	0.397
PtCo/HNGC-750	Initial	1.54	0.44	0.740	0.660
	After 5k	1.28	0.34	0.694	0.594
PtCo/HNGC-850	Initial	1.46	0.41	0.730	0.640
	After 5k	1.28	0.34	0.709	0.610
PtCo/HNGC-950	Initial	1.43	0.41	0.725	0.638
	After 5k	1.32	0.36	0.714	0.619

* The values were calculated from the current density at 0.9 $V_{iR\text{-}corrected}$. The total metal (PtCo) loading at the MEA cathode was 0.1 mg_{PtCo} cm^{-2} and the corresponding Pt amount was calculated from ICP-OES analysis in Table S5.

Table S7 Summary of the MEA results from commercial 20% Pt/C, PtCo/VC, and PtCo/HNGC-750 before and after 5k cycle accelerated durability test (ADT) for carbon support tested under H_2/Air.

Catalyst	Cycle number	P_{max} (W cm^{-2})	V @ 0.8 A cm^{-2} (V)	V @ 1.5 A cm^{-2} (V)
Commercial 20% Pt/C	Initial	0.66	0.645	0.403
PtCo/VC	Initial	0.71	0.657	0.474
	After 5k	0.25	< 0.2	-
PtCo/HNGC-750	Initial	0.78	0.659	0.511
	After 5k	0.62	0.607	0.413

Table S8 Estimated ohmic (R_{ohmic}), charge transfer (R_{ct}), mass transfer (R_{mt}) resistance from EIS data in Fig. S13.

Catalyst	R_{ohmic} (Ω cm^2)	R_{ct} (Ω cm^2)	R_{mt} (Ω cm^2)
PtCo/VC	0.080	0.934	0.232
PtCo/HNGC-750	0.078	0.808	0.192

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