Supporting Information

Highly nitrogen-doped mesoscopic carbons as efficient metal-free electrocatalysts for oxygen reduction reactions

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Table S1 HOMO-LUMO energy gap, spin density, and charge density of pure and N-doped graphene structures.

Type	Energy (eV)			Maximum spin density*	Maximum charge density*
	HOMO	LUMO	Gap		
Graphene (G)	-9.54	-6.65	2.89	0 (0%)	0.056 (~ 0%)
Pyrrolic-N (N5)	-8.50	-6.11	2.39	0.669 (4.8%)	0.168 (9.5%)
Pyridinic-N (N6)	-8.32	-6.24	2.08	0.290 (27.8%)	0.178 (11.1%)
Quaternary-N (NQ)	-6.81	-6.59	0.22	0.315 (13.0%)	0.223 (13.0%)
Pyridinic-N^+–O^- (NX)	-7.64	-6.27	1.37	0.192 (22.2%)	0.155 (11.1%)

* In unit of |e|. The values in parenthesis represent percentage of atoms with a spin or charge density greater than 0.15 |e| divided by the total number of atoms in the graphene structure (excluding H and N atoms).

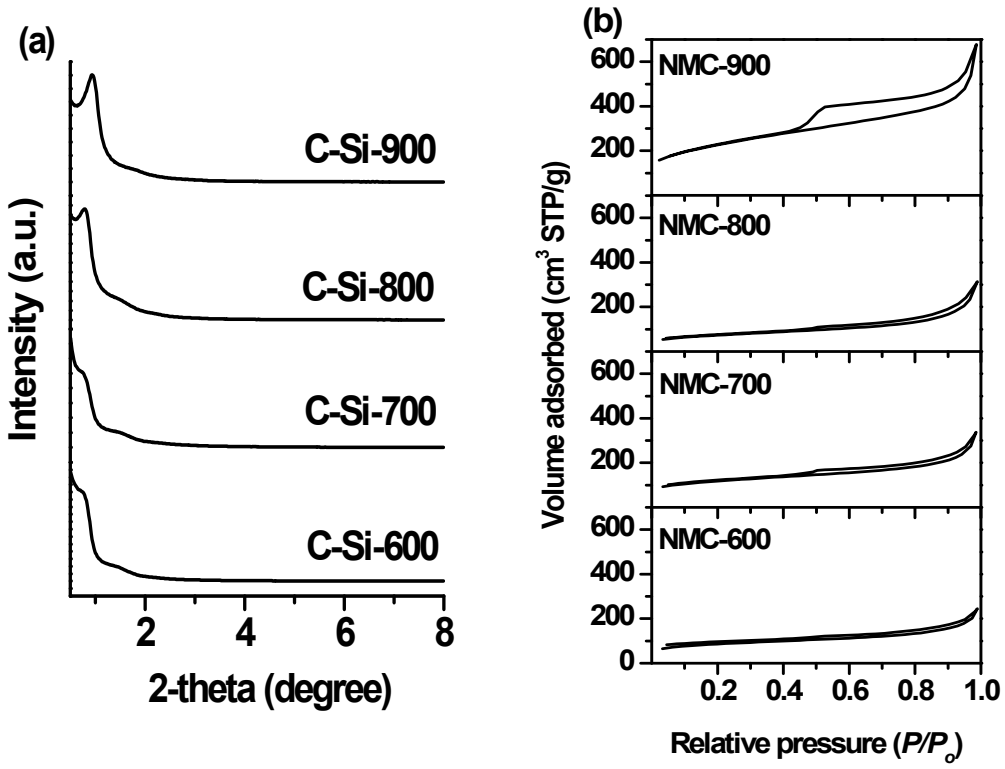

Fig. S1 (a) Small-angle XRD patterns of N-doped C-Si-T composites and (b) N_2 adsorption/desorption isotherms of NMC-T samples prepared with different carbonization temperatures (T = 600, 700, 800, and 900 °C) under microwave irradiation.

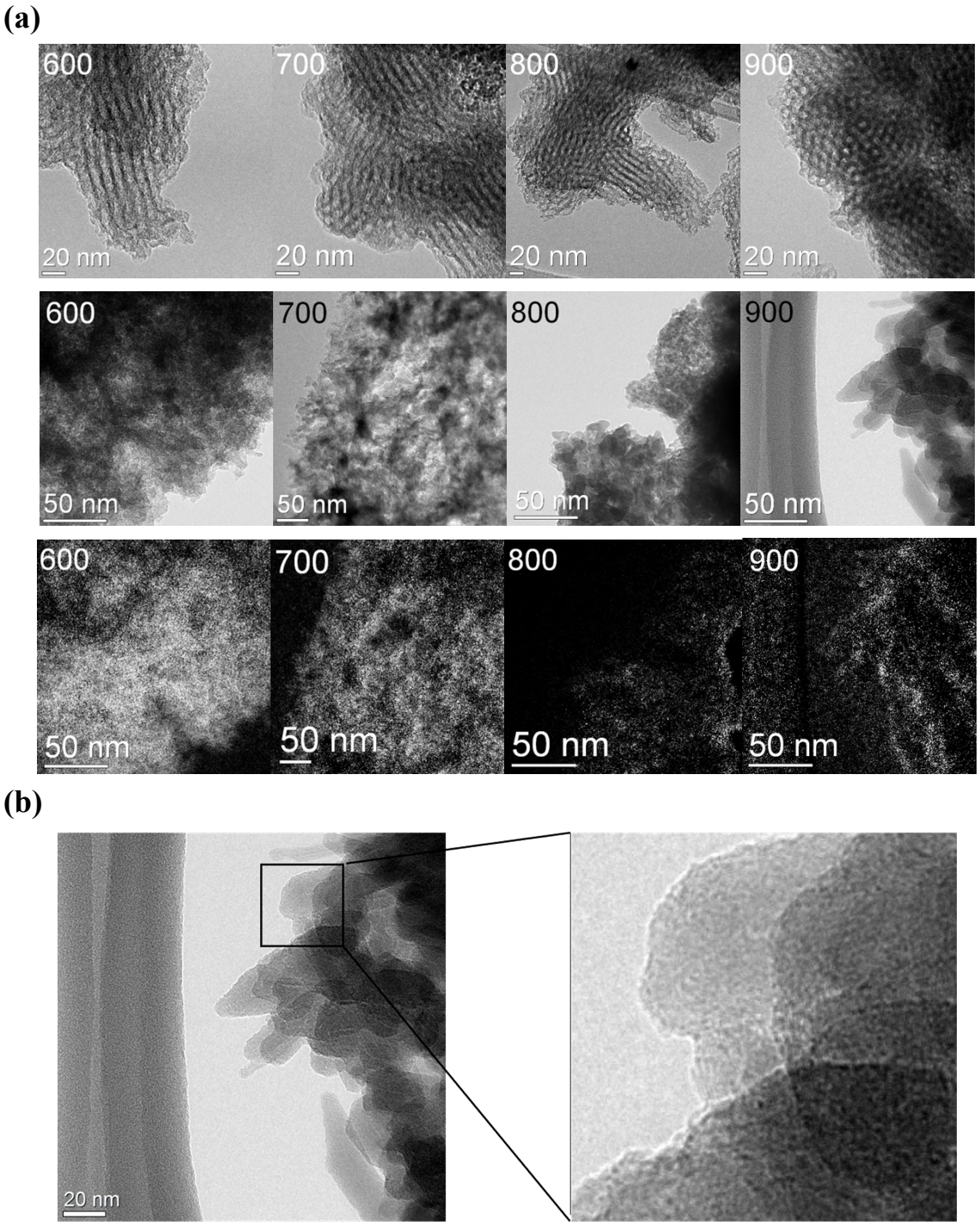

Fig. S2 (a) TEM images of various C-Si-T (Top) and NMC-T (middle) materials with varied carbonization temperature T ranging from 600 to 900 ^{o}C. Bottom: EELS N-mapping images of NMC-Ts, and (b) enlarged TEM image of NMC-900

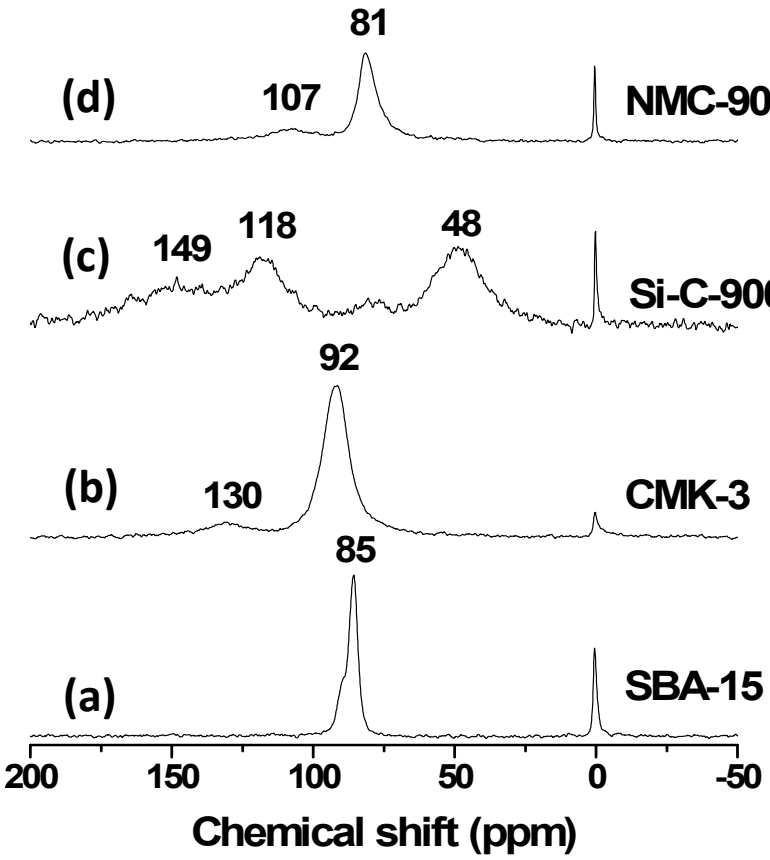

Fig. S3 Room-temperature ^{129}Xe NMR spectra of (a) ordered mesoporous silica SBA-15 and (b) its carbon replica (CMK-3). (c) C-Si-900, and (d) NMC-900. All spectra were recorded with a fixed xenon loading (equilibrium pressure 760 Torr) and same number of scans (NS) of 8,000 except for the Si-C-900, which was acquired with NS = 16,000. Similar to SBA-15 and CMK-3 with ordered mesostructures, the NMC-900 also shows existence of mesoporosities, as revealed by the peak at a ^{129}Xe chemical shift (δ) of ca. 81 ppm. Additional peak at $\delta \sim$ 107 ppm may be attributed to the presence of micropores. On the other hand, no mesoporosity was found for the Si-C-900 (before silica template removal); the substrate show only micropores ($\delta \sim$ 118 and 149 ppm) and very large pore ($\delta \sim$ 48 ppm); the latter is most likely arising from inter-particle voids.

Experimental details: all spectra were recorded on a Bruker-Biospin Avance-300 spectrometer operating at a Larmor frequency of 83.02 MHz using a single-pulse sequence with pulse-width of 3 μs and recycle delay of 2 s. The ^{129}Xe chemical shift was referred to that of dilute Xe gas (0 ppm).

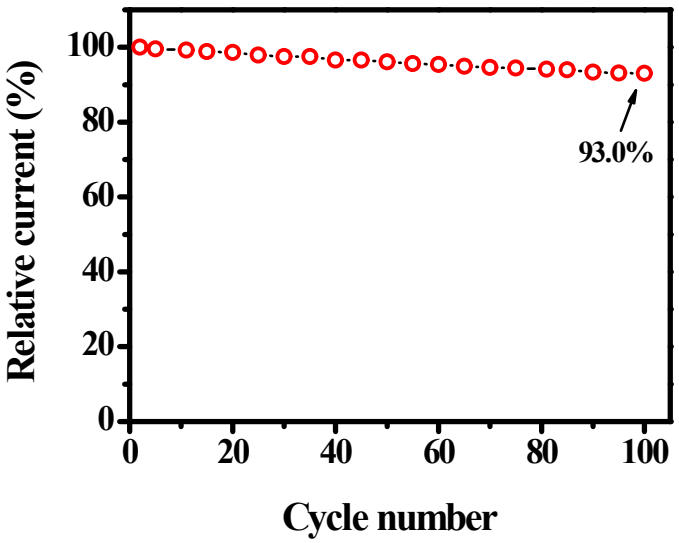

Fig. S4 Durability of NMC-900 up to 100 CV cycles. Only assorted results are shown for clarity reason. Relative currents were calculated based on oxygen reduction peak at –0.26 V.

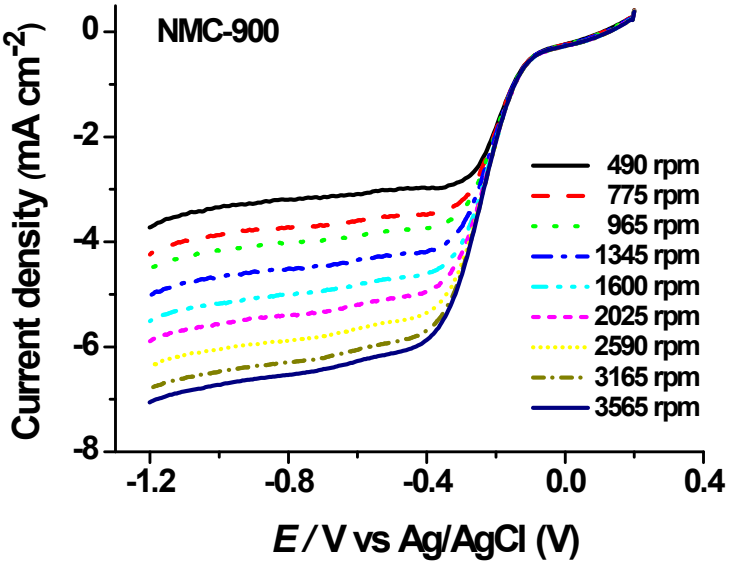

Fig. S5 Rotating disk electrode (RDE) voltammograms of NMC-900 supported GCE in O_2-saturated 0.1 M KOH solution recorded at a scan rate of 10 mV s^{-1} and varied rotation speeds (490 ~ 3565 rpm).

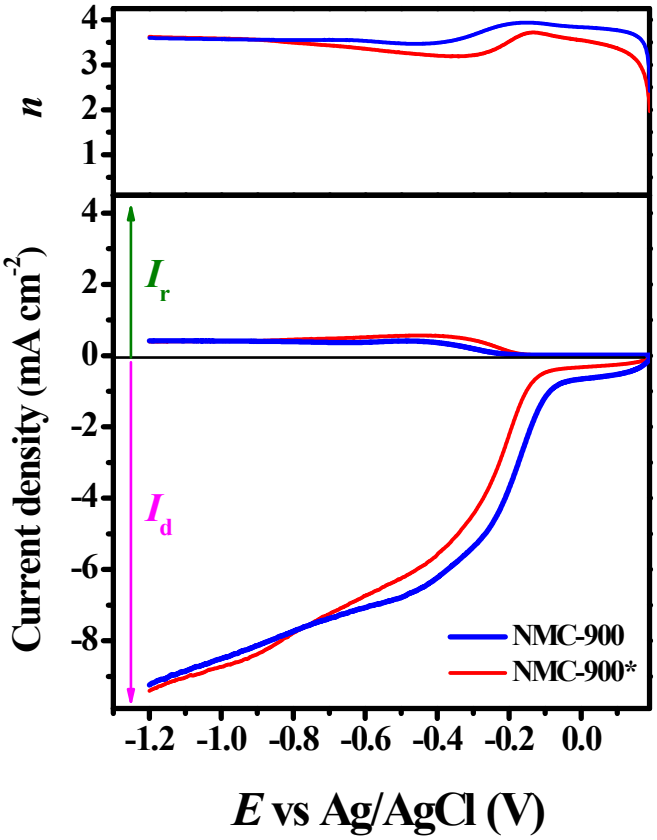

Fig. S6 Bottom: rotating ring-disk electrode (RRDE) of NMC-900 and NMC-900* in O_2-saturated 0.1 M KOH solution. Linear sweep voltammetry (LSV) was performed at a rotating speed of 1,600 rpm with a scanning rate of 50 mV s^{-1}, and the Pt ring electrode was polarized to oxidize the HO_2^- intermediates collected from the NMC modified glassy carbon (GC) disk electrode at 0.5 V. That the ring electrode current (I_r) is much less than disk electrode current (I_d), revealing little amount of hydroperoxide ion formation. Top: variations of electron transfer numbers (n) with potential calculated based on RRDE curves. A n value of 3.6 and 3.4 at −0.5 V may be inferred for NMC-900 and NMC-900*, respectively, in good agreement which the average n values calculated based on the rotating disk electrode (RDE) voltammograms (see Table 1).