Supporting information

Construction of hierarchical pores and pyridine nitrogen of metal-free catalyst for efficient oxygen reduction reaction

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Experimental Section

Materials and Instrumentation

Pt/C (20 wt%) was obtained from Alfa Aesar. And the other regents were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd., including magnesium chloride ($MgCl_2·6H_2O$), urea, nitric acid (HNO_3, 65 wt%), hydrochloric acid (HCl, 36 wt%) and potassium hydroxide (KOH). All the chemicals in this study were used without any further purification.

Nitrogen adsorption-desorption isotherms and pore size distributions were measured by a physical instrument of Autosorb IQ2 using Brunauer-Emmett-Teller (BET) and Density-Functional-Theory (DFT) method. Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) characterization were adopted by a JSM-7001F (JEOL Ltd.) and a JEM-2100F (JEOL Ltd.), respectively. The X-ray powder diffraction (XRD) patterns, Elemental analysis (EA) and X-Ray photoelectron spectroscopy (XPS) were characterized on a X'Pert3 Powder, a Vario EL CUBE and an AXIS ULTRA DLD, respectively. And the weight loss curve was measured by thermogravimetric analyzer in N_2 atmosphere with a heating rate of 10 ^oC/min.

Synthesis of the catalysts

The preparation method of oxidized asphaltene (AS(O)) was referred to previous work. AS(O), $MgCl_2·6H_2O$, and urea were dispersed and stirred in deionized water at 100 ^oC for 24. Then the solution was centrifuged at 12500 rpm for 10 min after

cooling down, and the resulted precipitate was marked as MT-100. The obtained MT-100 was pyrolyzed at 500 ^{o}C for 3 h (heating rate: 5 ^{o}C/min), and the pyrolysis product was named as MT-500. Finally, MT-500 was activated by KOH at 800 ^{o}C for an hour (N_2 atmosphere, 5 ^{o}C/min). After washing with 1 M HCl and distilled water, and the obtained sample was labeled as MTC-800. For comparison, the precursor AS(O) was directly activated by KOH and marked as AC-800.

Electrochemical measurements

Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were tested on a CHI 760E electrochemical workstation using a typical three-electrode electrochemical cell in 0.1 M KOH. A graphite rod, an Hg/HgO (saturated with KOH) and a glassy carbon (GC) disk (5.0 mm in diameter) were used as the counter electrode, reference electrode, and working electrode, respectively. All potential values were vs. RHE for comparison in this work：

$$E(vs.\,\mathrm{RHE}) = E(vs.\,\mathrm{Hg/HgO}) + 0.059 \times \mathrm{PH} + 0.098\ \mathrm{V} \tag{1}$$

The catalysts were dispersed in a mixture of ethanol and Nafion (5%) (volume ratio = 95:5) to form an ink with 5 mg/mL catalyst. Then 10 μL catalyst ink was deposited on the clean GC electrode surface and dried in air. The CV tests and LSV tests at different rotating speeds were conducted in Ar-saturated and O_2-saturated with a scan rate of 10 mV/s, respectively. Electron transferred number (n) was calculated by Koutecky-Levich (K-L) equation:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K} \tag{3}$$

where J, J_K, J_L and ω are the measured current density, kinetic current density, diffusion-limiting current density and electrode rotation speed in rpm, respectively; B is Levich slope calculated as following:

$$B = 0.2nFC_0D_0^{2/3}\nu^{-1/6} \tag{4}$$

where ν is the kinematic viscosity of the electrolyte (0.01 cm^2/s), F is the Faraday constant (96485 C/mol), C_0 is the concentration of O_2 (1.2×10^{-6} $molcm^3$), D_0 is the diffusion coefficient of O_2 in 0.1 M KOH, and n is transferred electron number in the

reduction of per O_2 molecule. The constant 0.2 is adopted when the rotation speed is expressed in rpm. The specific kinetic current density was obtained from K-L equation:

$$J_K = \frac{J_L \times J}{J_L - J} \tag{5}$$

where J, J_K and J_L are the measured current density, kinetic current density, diffusion-limiting current density, respectively.

The C_{dl} was obtained by cyclic voltammograms (CVs) at various scan rates (20-100 mV/s) over a potential windows of 0.198 to 0.298 V. Specifically, C_{dl} can be obtained by plotting the difference of anodic and cathodic current densities (ΔJ) at 0.25 V against the scan rates. The value of C_{dl} is half the slope of the above profiles. And the ECSA can be calculated as the following equation:

$$ECSA=C_{dl}/C_s \tag{6}$$

where Cs is the specific capacitance, and its value is 0.04 mF/cm^2 in alkaline media.

A primary Zn-air battery was fabricated with MTC-800 loaded on nickel foam as the air cathode (loading weight: 1.0 mg/cm^2), polished commercial Zn foil with a thickness of 0.2 mm as the metal anode, and 6.0 M KOH with the adding of zinc acetate (0.2 M) as the electrolyte. All the measurements were conducted on the as-constructed cell at room temperature with LANHE CT2001A electrochemical workstation (Shanghai Chenhua, China).

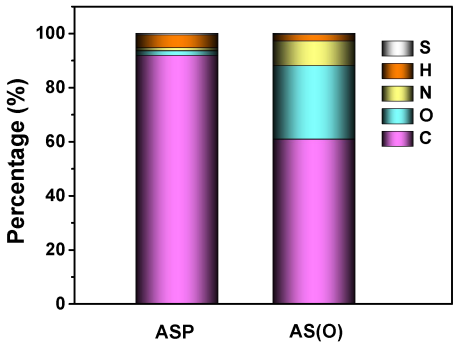

Figure S1 Histogram of elements of ASP and AS(O).

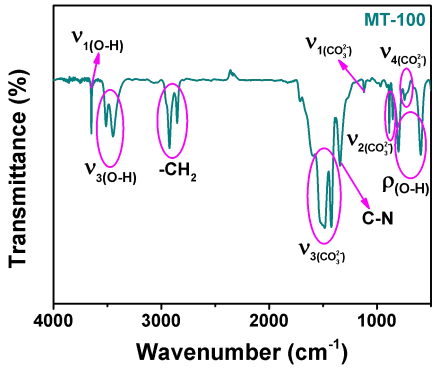

Figure S2. FT-IR spectrum of MT-100.

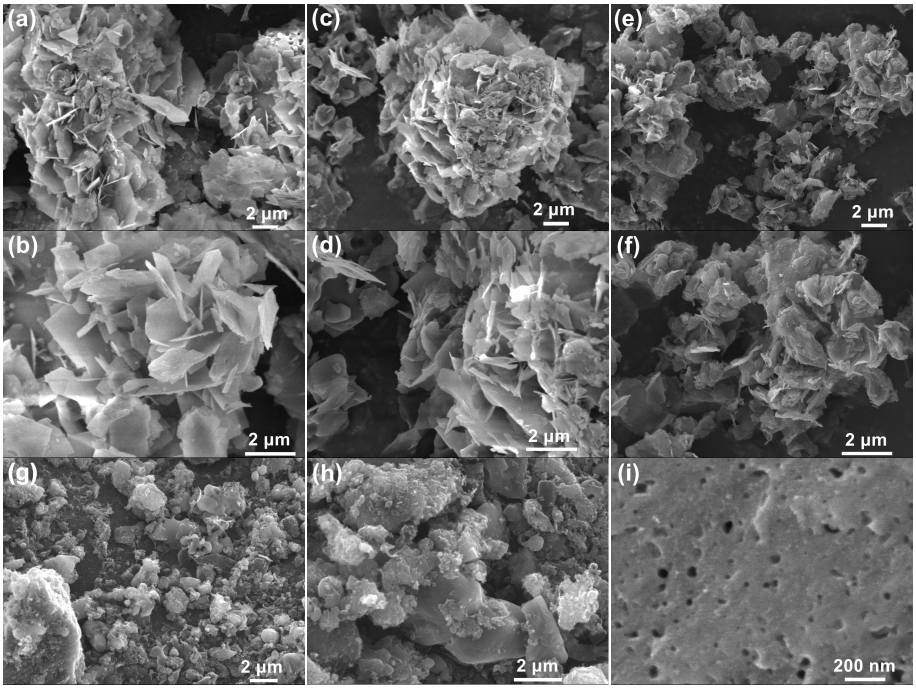

Figure S3. SEM images of (a,b) MT-100, (c, d) MT-500, (e, f, i) MTC-800, and (g, h) AC-800.

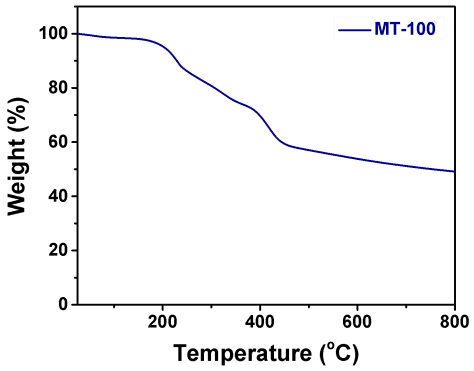

Figure S4. TG curve of MT-100 under N_2 flow. Heating rate: 10 °C/min.

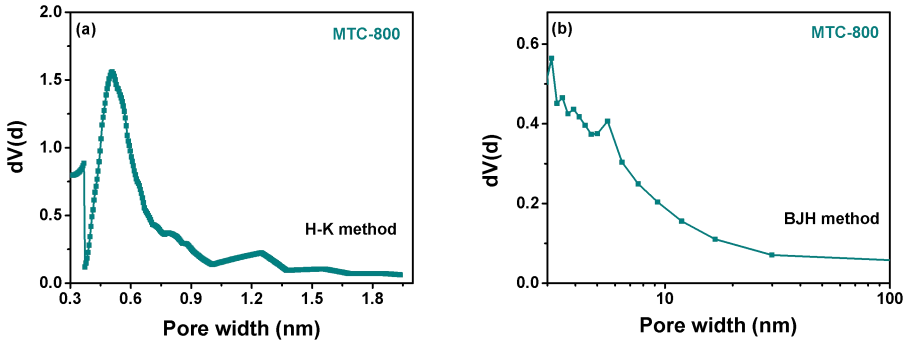

Figure S5. Pore size distribution of MTC-800 by (a) H-K and (b) BJH method.

Table S1 Physical parameters of MT-500, MTC-800 and AC-800

Samples	Specific surface area (m^2/g)			Pore volume (cm^3/g)		
	S_{BET}	S_{micro}	S_{meso}	V_{total}	V_{micro}	V_{meso}
MT-500	53	12	41	0.106	0.005	0.101
MTC-800	1511	1329	182	0.883	0.585	0.298
AC-800	1675	1621	54	0.789	0.680	0.109

[a]S_{BET} was measured by a Brunauer-Emmett-Teller method. V_{total} was calculated at a related pressure of 0.99. V_{meso} and S_{meso} were obtained by a Barrett-Joyner-Halenda (BJH) method.

Table S2 The chemical composition of MT-100, MTC-800 and AC-800 by EA

Samples	C (wt%)	H (wt%)	N (wt%)	O* (wt%)
MT-100	47.04	3.94	5.48	-
MTC-800	84.54	0.30	1.90	13.26
AC-800	78.03	0.77	1.29	19.91

O* content was calculated by the subtraction method.

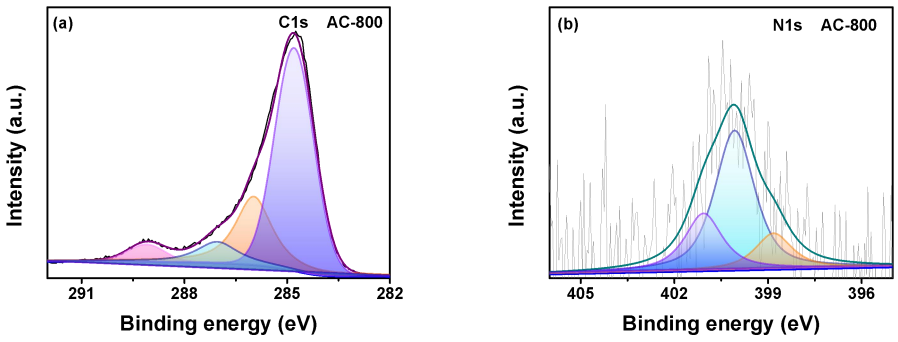

Figure S6. The C1s spectrum (a) and N1s spectrum (b) of and AC-800.

Table S3 The contents of the nitrogen functional groups based on XPS

Samples	N-6 (%)	N-5 (%)	N-Q (%)	amine/amide N (%)	protonated pyridine N (%)	nitrate (%)
MT-100	-	-	-	43.82	13.54	42.64
MTC-800	30.97	39.62	29.41	-	-	-
AC-800	15.33	59.66	25.01	-	-	-

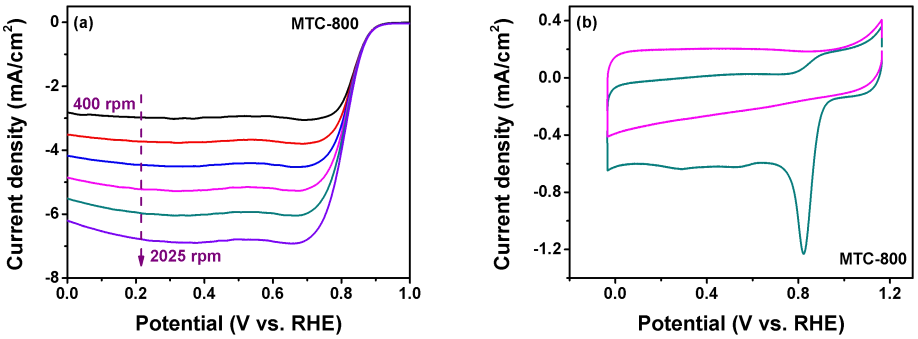

Figure S7. (a) LSV curves of MTC-800 at different rotation speeds; (b) CV curves of MTC-800 in Ar- and O_2-saturated electrolytes at a scan rate of 10 mV/s.

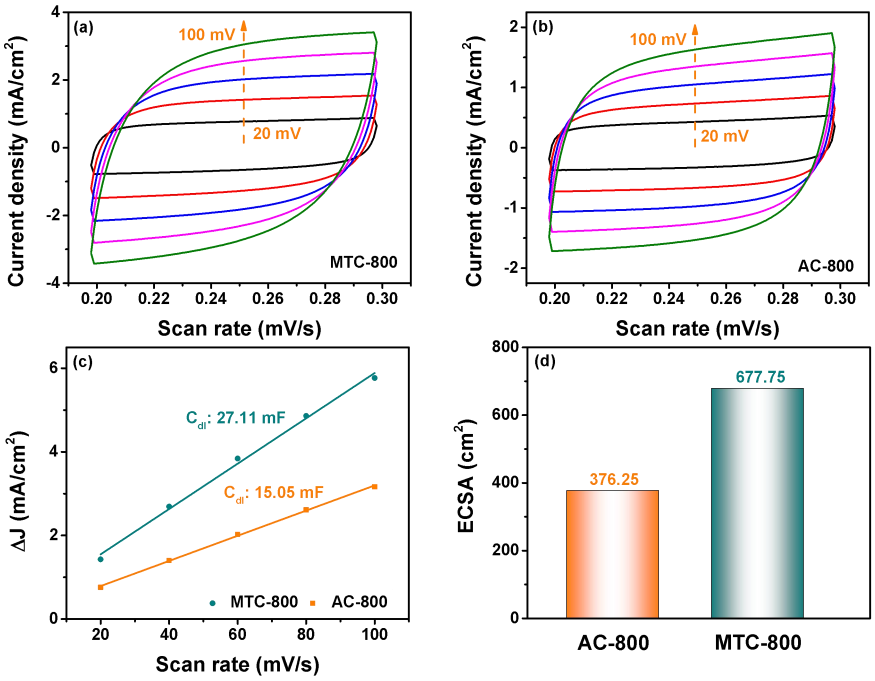

Figure S8. (a, b) CV curves at different scan rates of MTC-800 and AC-800, (c) plots of scan rate and current density based on CV curves, and (d) electrochemically active surface area (ECSA) of MTC-800 and AC-800.

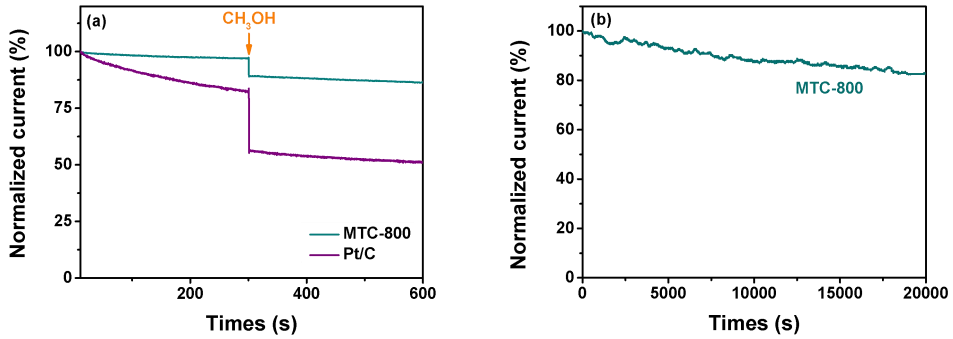

Figure S9. (a) Methanol crossover resistance test of MTC-800 and AC-800, and (b) durability test of MTC-800 in O_2-saturated 0.1 M KOH solution.

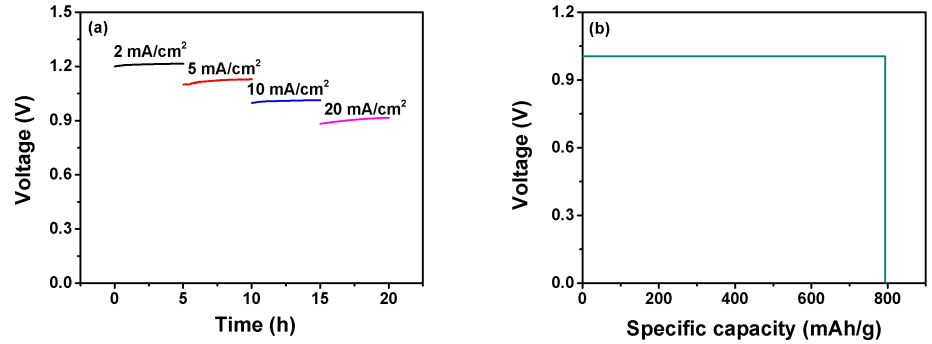

Figure S10. The properties of MTC-800-ZAB: (a) the galvanostatic discharge curves at different current densities, and (b) the galvanostatic discharge curve at 10 mA/cm^2 (specific capacities was obtained by normalized with the mass of consumed Zn).

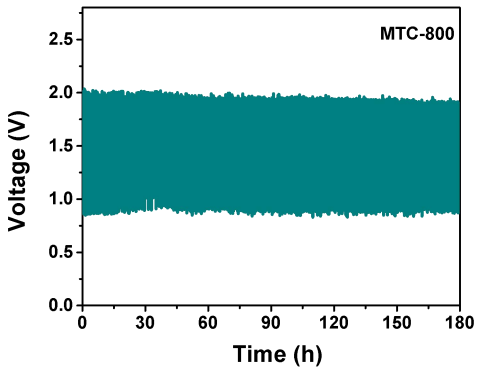

Figure S11. The cycling performance of MTC-800-ZAB at 5 mA/cm^2.