Electronic Supplementary Information

Hierarchically Porous Metal-free Carbon with Record-High Mass Activity for Oxygen Reduction and Zn Air Batteries

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Experimental details

Preparation of Poly-TA/β-CD. In an eggplant type flask, 15 mmol trithiocyanuric acid and 1 mmol β -cyclodextrin were dispersed into 30 mL DI water, followed by addition of 0.6 ml sulfuric acid. The mixture solution was sonicated for 30 min and then maintained in 100 °C for water full evaporation. Subsequently, the remaining solid was kept at 160 °C for 10 hours to polymerize β-cyclodextrin and cross-link trithiocyanuric acid. The obtained powder was then finely grinded and named as Poly-TA/β-CD.

Preparation of HPNSC catalyst from Poly-TA/β-CD. The as-obtained Poly-TA/β-CD was firstly heated from room temperature to 200 °C at a rate of 5 °C min⁻¹ for 1 hour, and then was heated up to 350 °C at a rate of 1 °C min⁻¹ for 2 hours, and was subsequently heated up to the desired temperature of 1000 °C for another 2 hours at a rate of 5 °C min⁻¹, while an Ar atmosphere at a flow

rate of 80 cm³ min⁻¹ was kept in the whole carbonization process. The as-prepared black powders are named as HPNSC.

Preparation of NSC catalyst from a physical mixture of TA and \beta-CD. For comparison, 15 mmol trithiocyanuric acid and 1 mmol β -cyclodextrin were grinded and mixed uniformly without further treatment. Then, the mixture powder was followed by the same carbonization process to obtain the black powder, named as NSC.

Structure Characterizations. The morphology structure of prepared catalysts was characterized by scanning electron microscopy (SEM), which were obtained on a S4700 SEM instrument by dropping the sample solutions onto a glass sheet and drying under ambient conditions. Transmission electron microscopic (TEM) and High Resolution Transmission Electron (HRTEM) images were obtained on the H800 instrument and the 2100F instrument. X-ray diffraction (XRD) measurements were performed with D/MAX 2000 X-ray diffractometer with Cu K α radiation (λ = 0.154178 nm) with 2 θ ranges from 5° to 80°. X-ray photoelectron spectroscopy (XPS) analysis was conducted with ESCALAB 250 (Thermo Fisher Scientific USA) equipped with an A1 Kalph 150W X-ray source. Raman spectra were collected by the Raman Spectroscopy (Renishaw), using 514 nm laser as the excitation source. The specific surface area and pore size distribution were characterized with a belsorp-max surface area detecting instrument (Tristar 3000) by N₂ physisorption at 77 K using the Barrett-Joyner-Halenda (BJH) method. We used the α s—plot method to calculate the surface area of micropores (Smic) and Kruk-Jaroniec-Sayari (KJS) method to yield a total mesopore surface area (Smes), so the remainder is ascribed to the macropore surface area (Smac).

Electrochemical Measurements. The electrochemical tests were carried out on a CHI 760e electrochemistry workstation in a three-electrode system. Simply, a glass carbon rotating disk

electrode coated with catalysts was used as working electrode, platinum sheet as counter electrode, saturated calomel electrode (SCE) as reference electrode and KOH solution (0.1 M) as the electrolyte. 5 mg catalyst was dispersed into 1 mL mixture solution of ethanol (950 µL) and Nafion (1 wt%, 50 μ L), then sonicated at least 30 min to form a homogeneous suspension. Then 10 μ L suspension was loaded onto a glass carbon electrode of 5 mm in diameter and dried at room temperature, resulting in a mass loading of about 0.25 mg cm⁻². A commercial Pt/C catalyst (20 wt%) was also coated on the glassy carbon electrode in the same way as a benchmark. In our electrochemical tests, all the potentials were calibrated to reversible hydrogen electrode (RHE, ERHE = ESCE + 0.241 + 0.059 pH). The catalyst on glassy carbon disk electrode was subjected to potential from 0 V to 1.0 V (vs. RHE) at a scan rate of 100 mV s⁻¹ for cyclic voltammetry (CV) measurements and 5 mV s⁻¹ for linear sweeping voltammetry (LSV) measurements with a rotating rate of 1600 rpm. The electrolyte was bubbled with high-purity O2 or N2 for 30 min before each test and maintained under O_2 or N_2 atmosphere during the measurements. Mass activity (Jm) was obtained by dividing kinetic current density (Jk) by total catalyst loading (m). Rotating ring-disk electrode (RRDE) measurements were also performed to investigate the electron transfer number of catalysts. Electrochemically active surface area (ECSA) of catalysts can be estimated and compared with their double layer capacitance (Cdl) values, since there is a direct correlation between Cdl, scan rate (v) and ECSA.(Adv. Mater. 2017, 29, 1604456.) The Cdl was calculated from doublelayer charging curves in a non-faradic potential range of 1.01 to 1.06 V vs. RHE. After linear fitting the current densities against scan rates, the slope is twice of Cdl. The electron transfer numbers (n), peroxide yields (H₂O₂%), kinetic current density (Jk) and ECSA were calculated by the following equations respectively:

$$n = 4 \times \frac{I_D}{I_D + I_R / N}$$
(SQ1)

$$H_2 O_2 \% = 200 \times \frac{I_R / N}{I_R / N + I_D}$$
(8Q2)

$$J_{K} = \frac{J \times J_{L}}{J_{L} - J}$$
(SQ3)

$$ECSA = \frac{C_{dl}}{C_{GC}}$$
(SQ4)

Where I_D and I_R are the disk and ring currents and N(0.37) is the ring collection efficiency, J is the measured current density, J_k and J_L are the kinetic current densities and diffusion-limiting current densities, CGC is the double layer capacitance of a glassy carbon electrode surface (0.2 F m⁻²),(J. Phys. Chem. C 2011, 115, 20002.) respectively.

Practical Battery Performance Evaluation. The improved ORR activity of HPNSC was further confirmed in a primary zinc air battery (PAFB) and a rechargeable zinc air flow battery (ZAFB). In PZAB, 2 mg HPNSC catalyst was loaded on a carbon paper over a square area 1 cm⁻² to achieve a catalyst loading of 2 mg cm⁻² with gas diffusion layer as air cathode, a polished Zn foil as the anode, and 8 M KOH and 0.5 M ZnO solution as the electrolyte. While in ZAFB, HPNSC together with commercial IrO_2 were loaded on gas diffusion layer coated carbon fiber paper as bifunctional oxygen electrode, a polished Zn foil as the anode, and 8 M KOH and 0.5 M ZnO solution as the electrolyte continuously flows through the electrode surfaces, which can prevent zinc dendrite formation and reduce the thermal management issue, which can

improve battery performance (especially for durability). The power density, charge-discharge polarization and stability tests were performed using a Land battery test system at room temperature.



Fig. S1. SEM images of (a) Poly-TA/ β -CD and (b) derived catalyst (HPNSC) at 1000 °C.



Fig. S2. SEM image of a physical mixture of TA and β -CD.



Fig. S3. XRD patterns of NSC catalyst.



Fig. S4. Raman spectra of HPNSC and NSC catalysts.



Fig. S5. Pore volumes of micropores, mesopores, macropores and total pores of HPNSC and NSC catalysts.



Fig. S6. Cyclic voltammogram curves of (a) HPNSC and (b) NSC, and (c) corresponding linear fitting of capacitive current.



Fig. S7. (a) XPS survey spectra of HPNSC and NSC catalysts, corresponding (b) N1s and (c) S2p high resolution spectra.



Fig. S8. Cyclic voltammogram curves of HPNSC and NSC in N_2 -saturated and O_2 -saturated solution with 0.1 M KOH at a scan rate of 5 mV s⁻¹.



Fig. S9. Electrochemical AC impedance spectra of HPNSC and NSC.



Fig. S10. Methanol tolerance of HPNSC and commercial Pt/C.



Fig. S11. Discharge voltage curves of primary zinc air battery at 5 mA cm⁻², 10 mA cm⁻², 20 mA cm⁻² and 40 mA cm⁻², respectively.



Fig. S12. Charge and discharge voltage curves of ZAFB at constant current density of 10 mA cm⁻²

for 2 hours per cycle and 20 mA cm $^{-2}$ for 1 hour per cycle.

Catalysts	Mass activity (J _k /m)@ V	Electrolyte	Ref.
HPNSC	126.7 @0.8V 35 @0.85V	0.1M KOH	This work
N,P-MC	17.35@0.85V	0.1M KOH	ACS Appl. Mater. Interfaces 2017, 9, 16236
ENG	2.6@0.85V	0.1M KOH	J. Solid State Electrochem. 2017, 21 , 128
Meso/micro-PoPD	35@0.85V	0.1M KOH	Nat. Commun. 2014, 5, 4973
NPOMC-L1	26.57@0.8V	0.1M KOH	Angew. Chem. Int. Ed. 2015, 54, 9230
HNS-800	90.1@0.8V	0.1M KOH	React. Chem. Eng. 2018, 3, 238
N-MCNs-7-900	7.5@0.8V	0.1M KOH	Angew. Chem. Int. Ed. 2015, 54 , 15191
WHC-700	5.78@0.8V	0.1M KOH	Nanoscale 2015, 7, 6136
THNC-800	26.89@0.8V	0.1M KOH	ChemElectroChem 2015, 2, 803
NDGs-800	68.19@0.8V	0.1M KOH	ACS Energy Lett. 2018, 3 , 1183
MPSA/GO-1000	56.33@0.65V	0.1M KOH	Angew. Chem. Int. Ed. 2016, 55, 2230
MEP-NC850	15.2@0.75V	0.1M KOH	Electrochim. Acta 2017, 257 , 73

 Table S1. Mass activities of HPNSC and recently reported metal free carbon catalysts.