Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Supporting Information

Controlled synthesis of porous nitrogen-doped carbon nanoshell for highly efficient oxygen reduction

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Experimental section

Matertials

All chemicals used in the synthesis of electrocatalysts are analytical reagents (AR). 1,10-phenanthroline-5,6-dione and 1,2,4,5-benzenetetramine tetrahydrochloride were bought from Beijing HWRK Chem Co., Ltd. Ferric trichloride ($FeCl_3$), and N, N-dimethylformamide (DMF) were bought from J&K Chemical Technology. Anhydrous ethanol and hydrofluoric acid (HF) were purchased from Beijing Chemical Works. Nafion were supplied by DuPont Company, respectively. Commercial Pt/C catalyst was bought from Alfa Aesar Chemical Co., Ltd. High-purity argon (99.99%) gas was obtained from Beijing AP BAIF Gases Industry Co., Ltd.

Synthesis of 9,11,20,22-tetraaza-tetrapyridopentacene (tatpp)

The tatpp sample was synthesized according to the previous report with slight modification.[1] A mixture of 1,10-phenanthroline-5,6-dione (1.50 g, 7.2 mmol), 1,2,4,5-benzenetetramine tetrahydrochloride (1.02 g, 3.6 mmol), potassium acetate (0.99 g, 7.2 mmol) was suspended in the mixture of ethanol (120 mL), and refluxed under nitrogen for 24h. After cooling of the reaction to room temperature, the precipitate was filtered out and washed with 75 mL of boiling ethanol and 75 ml of hot water. Then, the crude product was depurated by Soxhlet extraction method for 60 h and finally dried in vacuum at 60 °C.

Preparation of HNS-T catalysts. The HNS-T catalysts was synthesized by pyrolysis of iron-complex precursor and leaching with hydrofluoric acid. The detail can be found as below. To synthesize iron-complex precursor, a mixture of tatpp (0.05 g, 0.1 mmol) and $FeCl_3$ (0.025 g, 0.15 mmol) was suspended in 30 ml N, N-dimethylformamide, which was then added to the suspension of disperse silica nano-spheres (0.5 mg ml^{-1},120 ml) under ultrasound, after 30 min of ultrasound, the mixture was transferred into a Teflon-lined stainless autoclave, after placement in an oven at 180 ºC for 24 h, the brown product was collected by centrifugation, then washed with DMF and ethanol for several times and dried in vacuum at 60 ºC overnight. Finally, the precursor was pyrolyzed in a quartz tube at 800 ºC (700, 900ºC) for 2 h under argon atmosphere, and then leached in 10% hydrofluoric acid (HF) for 8 h to remove silica spheres, the leached sample was washed to neutral with water for several times and dried in vacuum at 60 ºC overnight, and then the product was denoted as HNS-800(700,900).

Preparation of NR-T catalysts. The NR-T catalysts was synthesized similar to the above HNS-T catalysts without SiO_2 spheres as the template.

Physical characterization. Powder X-ray diffraction (PXRD) measurements were recorded on D/MAX 2000 X-ray diffractometer with Cu Kα line (λ=1.54178 Å) as the incident beam. X-ray photoelectron spectroscopy (XPS) analysis was obtained on ESCALAB 250 operated at 150W and 200 eV with monochromated Al Kα radiation. BET data were gained on ASAP 2020 V3.04 H. Liquid-state NMR spectra were measured on a Bruker AV600 spectrometer operating at 600 MHz for ^{1}H. Scanning electron microscopic (SEM) images were performed on a S4700 SEM instrument. Transmission electron microscopic (TEM) and High Resolution Transmission Electron Microscopy (HRTEM) images were obtained on the H800 and the 2100F instrument.

Electrochemical Evaluation. All the electrochemical measurements were carried out in a conventional three-electrode cell using CHI760E electrochemical workstation controlled equipped with a glassy carbon rotating disk electrode (RDE) at room temperature. Glassy carbon (GC) electrodes (5.61mm diameter, PINE instrument Inc.) were polished with a 0.5, 0.15 and 0.05 µm alumina slurry (CH Instrument Inc.) in turn and subsequently rinsed with ultrapure water and ethanol. The counter electrode and reference electrode were a Pt ring and saturated calomel electrode, the potential versus reversible hydrogen electrode (E_{RHE}) was converted from potential versus SCE (E_{SCE}) following the Nernst equation $E_{RHE} = E_{SCE} + 0.059\times$ (pH) + 0.242

Preparation of the Electrode. 5 mg of electrocatalyst was ultrasonically dispersed in 50 µL of Nafion solution (0.5 wt.%) and 0.95 mL of anhydrous ethanol for about 30 minutes to form a homogeneous ink. Then, 10 µL of the as-prepared catalyst ink (containing 50µg of catalyst) was dropped on a glassy carbon rotating disk electrode giving a loading of 0.2 mg cm^{-2}. The commercially carbon-supported Pt/C electrode was prepared according to the above procedure with loading of ~0.2 mg cm^{-2}.

Electrochemical measurements. The cyclic voltammetry (CV) measure-ments (using a CHI 760E) were conducted in O_2-saturated 0.1 M KOH or 0.1 M $HClO_4$ electrolyte using saturated calomel electrode as the reference electrode, 0.1 cm^2 platinum foil as the counter electrode and the electrocatalyst modified glassy carbon electrode as the working electrode. Electrolyte was saturated with high-purity oxygen at room temperature by bubbling O_2 prior to the measurements for at least 30 mins. Meanwhile, a flow of O_2 was maintained over the electrolyte during the recording of CVs. The working electrode was cycled at least 20 times before the datas were recorded at a scan rate 100 mV·s^{-1} from 0 to 1.2 V vs reversible hydrogen electrode (RHE). In control experiments, CV measurements were performed in a N_2 saturated electrolyte. In RDE experiments, the potential was cycled from 1.1 V to 0 V (vs RHE) at a scan rate 5 mV s^{-1} with the electrode rotation speed of 1600 rpm to record the polarization curves. The RDE tests are conducted at different rotating speeds from 400 to 1600 rpm, and the

Koutecky–Levich (K–L) plots are obtained from polarization curves at different potentials. The fitting linearity of the K–L plots indicates first-order reaction kinetics toward the electron transfer numbers for ORR at different potentials. The following equations.

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

$$B=0.62nFC_0(D_0)^{2/3}v^{-1/6}$$

where J is the measured current density, J_K and J_L are the kinetic- and diffusion-limiting current densities, ω is the angular velocity of the electrode rotating, n is transferred electron number per oxygen molecule, B is the reciprocal of the slope, F is the Faraday constant (F = 96485 C mol^{-1}), C_0 is the bulk concentration of O_2 (1.2×10^{-3}mol L^{-1}), D_0 is the O_2 diffusion coefficient (1.9×10^{-5} cm^2 s^{-1}), v is the kinematic viscosity of the electrolyte (1×10^{-2} cm^2 s^{-1}). The constant 0.62 is adopted when the rotation speed is expressed in rad s^{-1}.

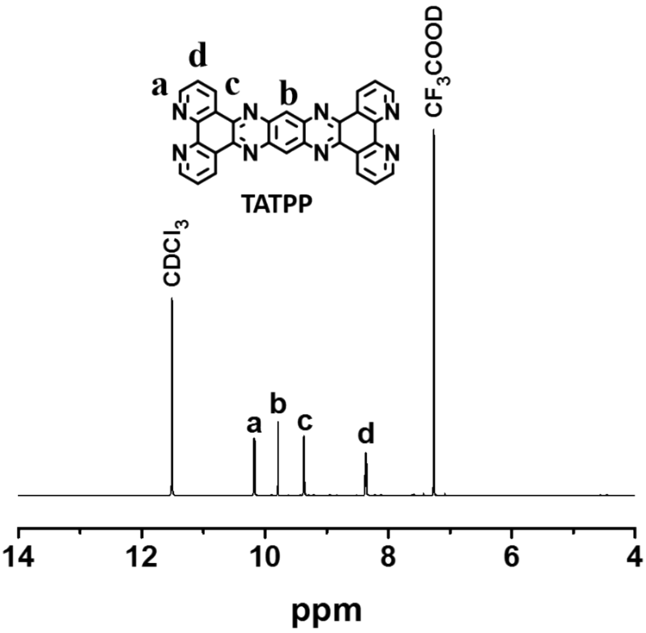

Figure S1. The Liquid-state ^{1}H NMR spectrum of the as-synthesized tatpp in the mixture of $CDCl_3$ and CF_3COOD (9:1), The resonance peaks at 10.20, 9.79, 8.36 and 8.33 ppm represent four different types of hydrogen, respectively.

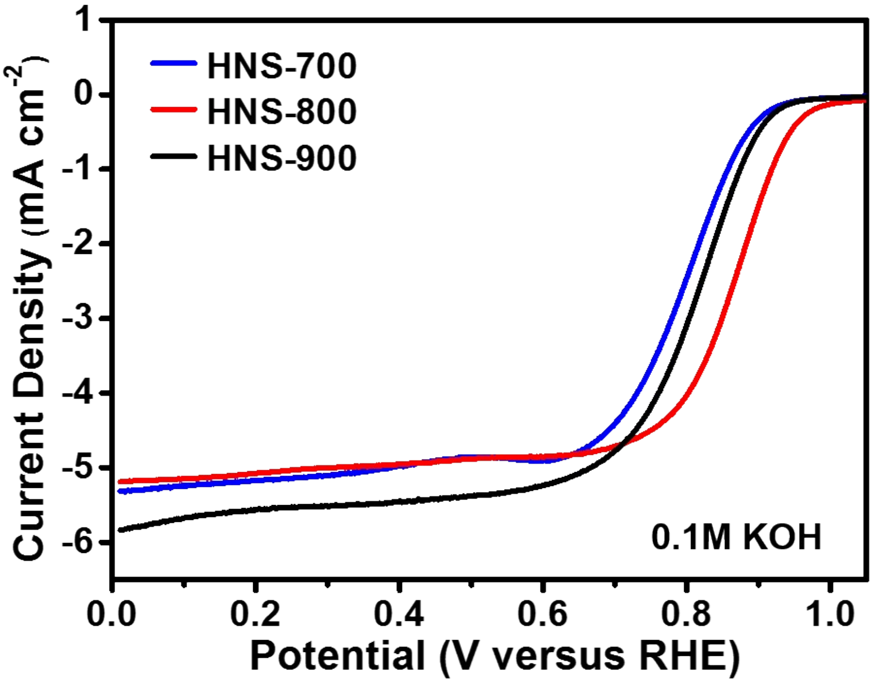

Figure S2. The LSV curves of HNS-700, HNS-800 and HNS-900 in O_2-saturated 0.1 M KOH solution at a scan rate of 5 mV s^{-1} and a rotation speed of 1600 rpm.

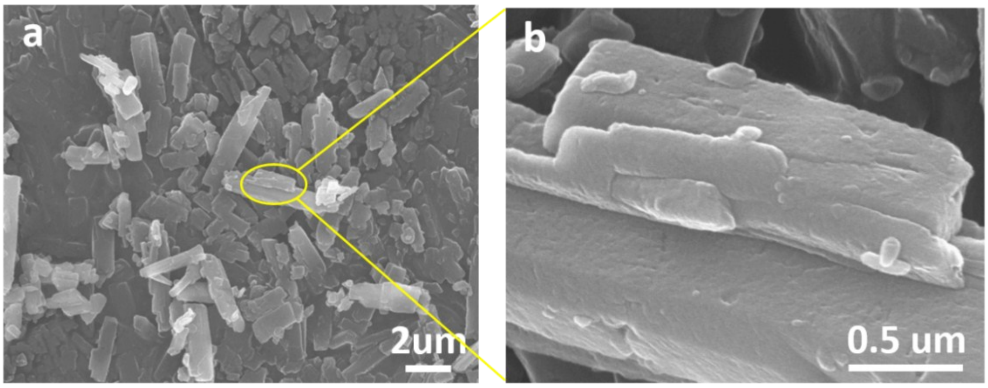

Figure S3. SEM images of the control sample nanorod (a) low magnification and (b) high magnification.

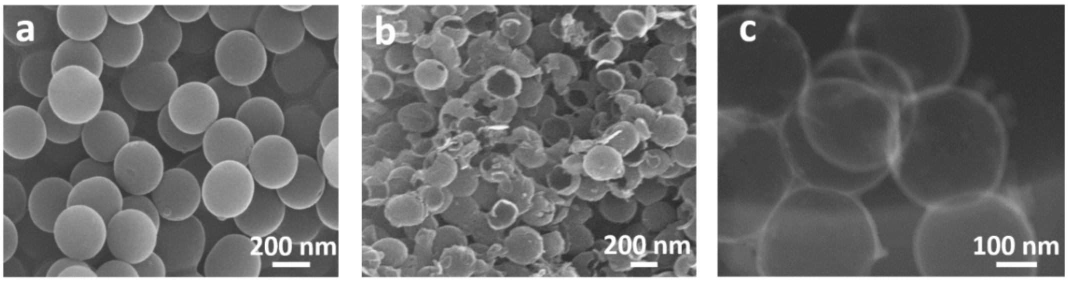

Figure S4. (a and b) SEM images of silica nano-spheres and HNS-800 catalysts, (c) HRTEM image of HNS-800.

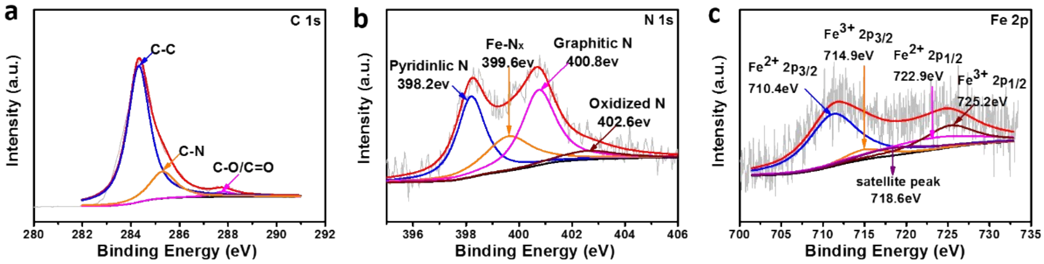

Figure S5. XPS spectra of NR-800 catalysts: (a) the C 1s spectrum, (b) the N 1s spectrum, and (c) the Fe 2p spectrum.

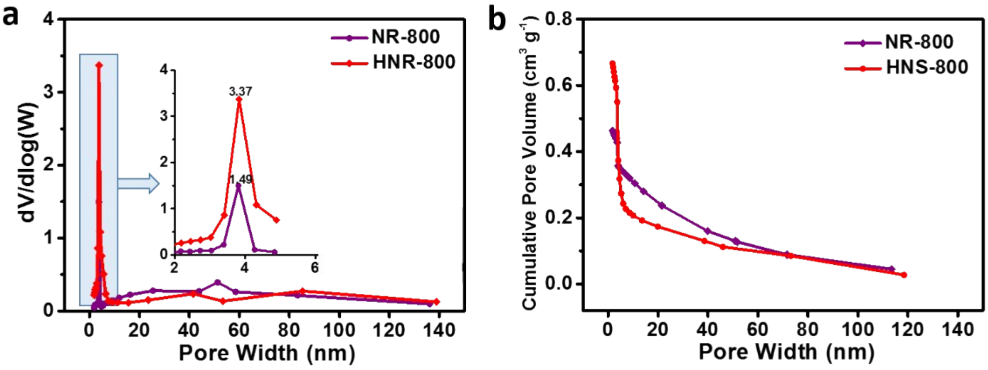

Fig S6. (a) BJH dV/dlog (W) pore volume distribution, where V is pore volume and W is pore width. The micropore size distribution had obvious peaks associated with the pore widths: 3.83nm of HNS-800, 3.81nm of NR-800. (b) BJH cumulative pore volume of NR-800 and HNS-800 catalysts.

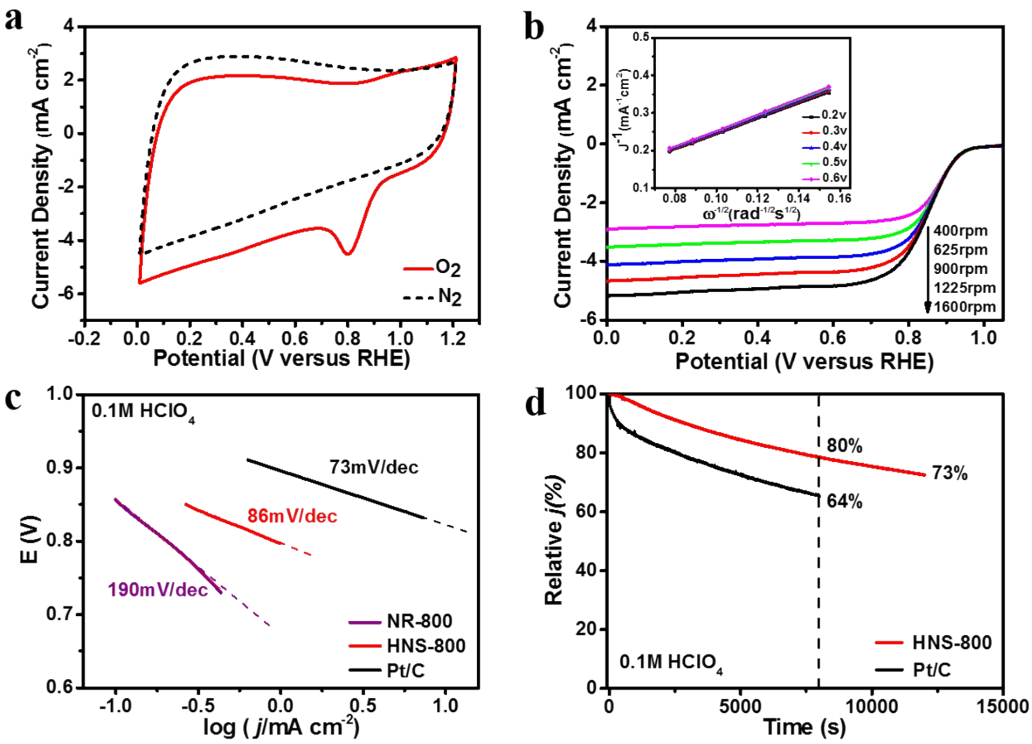

Fig S7. (a) Cyclic voltammograms of HNS-800 in O_2-saturated and N_2-saturated 0.1M KOH on glassy carbon electrodes at a scan rate of 100 mV s^{-1}. (b) LSV curves of HNS-800 at different rotation speeds and inset showing the corresponding K-L plots. (c) Tafel plots of different catalysts at a scan rate of 5 mV s^{-1} with 1600 rpm in 0.1M $HClO_4$ solution. (d) the chronoamperometric curves of HNS-800 and Pt/C electrodes at 0.6 V and a rotation speed of 1600 rpm in 0.1M $HClO_4$ solution.

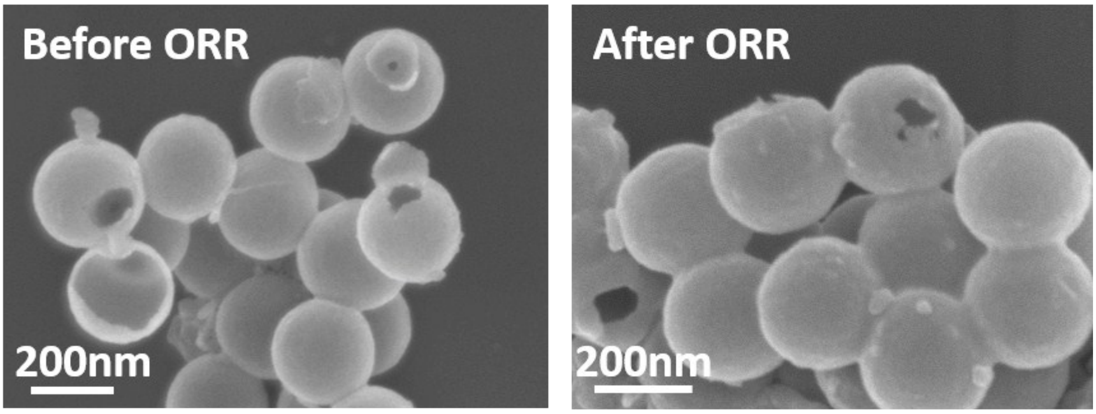

Figure S8. SEM images of HNS-800 catalysts after ORR treatment without obvious morphology change

REFERNCES

1 M. J. Kim, R. Konduri, H. Ye, F. M. MacDonnell, F. Puntoriero, S. Serroni, S. Campagna, T. Holder, G. Kinsel and K. Rajeshwar, *Inorg. Chem.*, 2002**, 41**, 2471.