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Electronic Supplementary Information

Biochemistry-Inspired Direct Synthesis of N,P-Codoped Microporous Carbon Nanospheres for Enhanced Electrocatalysis

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1. Experimental Section

1.1 Chemicals.

Dopamine hydrochloride (DA) was purchased from Beijing J&K Scientific Co., and F127 was purchased from Nanjing Well Chemical Co., Ltd. Sodium salt hydroxyethylidene diphosphonic acid (HEDPS) was obtained from Henan Qingyuan Chemical Co. All of chemicals were of analytical grade without any further purification.

1.2 Material Synthesis.

NP-MCS. In a typical run, F127 was first dissolved in a mixture of deionized water and ethanol with volume ration of 1:2, and a colorless solution was obtained after stirring for 20 min. After 2 hour of stirring, HEDPS was dissolved in the mixed solution, followed by the slow addition of dopamine, and the pH value of the mixture was 8.5. The molar ratio of F127:dopamine:HEDPS is 2:10:5. After the addition of HEDPS, the polymerization of dopamine monomers slowly occurred, accompanied with a color change of the solution from colorless to pale brown, and finally turning to deep brown with passing time. After 24 h continuous stirring, the polymeric product was collected by centrifugation, washed with water and dried at 80 °C for 12 h in vacuum Carbonization was carried out in a tubular furnace under an inert atmosphere (N_2 flow), keeping at the 700 °C for 3 h. Finally, microporous N,P-doped carbon spheres with uniform spherical size were obtained.

N-MCS. For comparison, microporous N-doped carbon spheres were prepared with the use of traditional buffer reagent, 10mM *tris*–HCl (pH = 8.5), instead of HEDPS. The other procedures were same to that for NP-MCS.

1.3 Characterization.

Scanning electron microscopy (SEM) was carried out on a Jeol JSF-7500L microscope at 5 kV. Transmission electron microscopy (TEM) was carried out on a Jeol JEM 2100F microscope at 200 kV. All samples subjected to TEM measurements were ultrasonically dispersed in ethanol and dropcast onto copper grids covered with a carbon film. N₂ adsorption–desorption isotherms were measured on an Autosorb-1 sorption analyzer (Quantachrome) at liquid nitrogen temperature (77 K). Prior to measurement, the samples were degassed at 200 °C overnight. Surface areas were calculated by the multi-point Brunauer–Emmett–Teller (BET) method; total pore volumes were estimated from the volume adsorbed at a relative pressure (P/P_0) of 0.995; the pore-size distribution was calculated from the adsorption branch using the Quenched Solid Density Functional Theory (QSDFT) method. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Focus Diffractometer with Cu-K α radiation ($\lambda = 0.15418$ nm) operated at 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos Axis Ultra DLD (delay line detector) spectrometer equipped with a monochromatic Al-K α X-ray source (1486.6 eV). All XPS spectra were recorded using an aperture slot of 300 × 700 microns, survey spectra were recorded with a pass energy of 160 eV and high resolution spectra with a pass energy of 40 eV. Raman spectra were obtained on Thermo-Fisher Scientific DXR spectrometer with 532 nm wavelength incident laser light.

1.4 Electrode preparation and electrocatalytic activity evolution.

To prepare the working electrode, 6 mg NP-MCS were dispersed in a mixed solution containing 0.8 mL Mill-Q water and 0.2 mL isopropanol under sonication. 8 μ L of the obtained homogeneous catalyst ink was dropped onto a polished GC electrode. Following overnight solvent evaporation under ambient conditions, a thin layer of Nafion[®] solution was coated onto the electrode surface and then dried in air, and the resulting electrode was utilized as a working electrode. All the electrochemical measurements were conducted in a three-electrode configuration. Ag/AgCl was used as the reference electrode and the counter electrode was platinum wire. The resultant potentials were referenced to a reversible hydrogen electrode (RHE) by adding a value of (0.205 + 0.059 × pH) V. Pt/C (20 wt%, Alfa Aesar) electrode was prepared by using the same procedure. Electrochemical experiments were conducted at room temperature on a CHI660D electrochemical workstation (CH instrument Co., USA).

For the typical ORR tests, a flow of O_2 was maintained over the electrolyte (0.1 M KOH) during the recording of electrochemical measurements in order to ensure its continued O_2 saturation.

Cyclic voltammograms (CVs) and linear sweep voltammograms (LSVs) were carried out using a RDE. The scan rate of CVs was kept as 20 mV s⁻¹ while that for LSVs was 5 mV ⁻¹. All the electrochemical data were recorded after contiguous CV cyclic scans at a rate of 50 mV s⁻¹ for at least 50 times. On the basis of RDE data, the overall electron transfer number per oxygen molecule involved in oxygen reduction can be determined by Koutechy-Levich (K-L) equation:

$$1/J = 1/J_{\rm k} + 1/J_{\rm L} = 1/J_{\rm k} + 1/B\omega^{1/2}$$

where J_k is the kinetic current and ω is the electrode rotating rate. *B* is determined from the slope of the K-L plots based on the Levich equation as given below:

$$B = 0.2nF(D_{\rm O2})^{2/3}v^{-1/6}C_{\rm O2}$$

where *n* represents the transferred electron number per oxygen molecule. *F* is Faraday constant ($F = 96485 \text{ C mol}^{-1}$). D_{O2} is the diffusion coefficient of O_2 in 0.1 M KOH. *v* is the kinetic viscosity. C_{O2} represents the bulk concentration of O_2 . The constant 0.2 is adopted when the rotation speed is expressed in rpm.

For the typical HER measurements, linear sweep voltammetry with scan rate of 2 mV s⁻¹ was taken in 0.5 M H₂SO₄ continuously purged with hydrogen using a rotating disc electrode with a rotating rate of 1600 rpm during the test so as to remove hydrogen gas bubbles formed at the catalyst surface. The onset potential of the catalyst was obtained on the basis of the beginning of the linear part of the Tafel plots. All polarization curves were corrected for the *iR* compensation within the cell.

2. Supplementary Figures



Fig. S1 Structures of HEDPS under different pH conditions.



Fig. S2 FT-IR spectrum of PDA and HEDPS-incorporated PDA. As to HEDPS-incorporated PDA, the presence of weak P-OH vibration band and weakened amine groups as compared with pristine PDA suggest the successful introduction of organophosphonic linkages.



Fig. S3 SEM images of NP-MCS and the corresponding EDS mapping of C, N and P.



Fig. S4 Wide Angle XRD pattern of the NP-MCS material.



Fig. S5 (a) SEM and (b) TEM images of the N-MCS sample.



Fig. S6 XPS survey and high-resolution spectra of C 1s, N 1s and P 2p core levels in N-MCS. It can be found that P cannot be introduced into N-MCS without the assistance of HEDPS.



Fig. S7 (a) N_2 adsorption-desorption isotherm of NP-MCS and N-MCS and (b) the corresponding pore size distribution curves. The total pore volume for NP-MCS and N-MCS are determined to be 0.428 and 0.387 cm³ g⁻¹, respectively.



Fig. S8 N_2 adsorption-desorption isotherm of the carbonaceous material prepared in the absence of F127. The specific surface area is determined to be 313 m² g⁻¹.



Fig. S9 (a) ORR polarization curves of NP-MCS at different rotating speeds. (b) K-L plots at 0.4 V.



Fig. S10 (a) ORR polarization curves of Pt/C at different rotating speeds. (b) K-L plots at 0.4 V.



Fig. S11 LSV polarization cuves on RDE for Pt/C standard in O_2 -saturated 0.1 M KOH and with 1 M methanol at a rotating speed of 1600 rpm. The ORR curve for Pt/C electrode manefests a weak oxidation peak between 0.8 V in the presence of methanol, which could be ascribed to the oxidation of methanol. In addition, Pt/C electrode shows a negative on-set potential shift for ORR with the addition of methanol.



Fig. S12 LSV polarization cuves on RDE for NP-MCS electrode in O₂-saturated 0.1 M KOH and with 1 M methanol at a rotating speed of 1600 rpm. No significant variations of the ORR curves can be detected for the NP-MCS electrocatalyst in the presence of methanol.



Fig. S13 (a) LSV polarization cuves on RDE for NP-MCS and N-MCS in 0.5 M H_2SO_4 at a rotating speed of 1600 rpm and scan rate of 2 mV s⁻¹. (b) Tafel plots of the synthesized carbonaceous materials.



Fig. S14 Chronoamperometric response for NP-MCS measured at a potential of -0.27 V.