Porous Organic Polymers as Fire-Resistant Additives and Precursors for Hyperporous Carbon towards Oxygen Reduction Reactions

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Section 1. Materials and Methods

N\textsubscript{2} adsorption/desorption measurements were conducted at low temperature of 77 K via Micromeritics ASAP 2020 surface area and porosimetry analyser. Before test, all samples were initially degassed overnight under high vacuum at the temperature of 150\textdegree{}C. Thermal gravimetric analysis (TGA) was examined using NETZSCH STA 449C analyzer at the temperature ranged from 30\textdegree{}C to 800\textdegree{}C with a heating rate of 10 \textdegree{}C min\textsuperscript{-1} under the protection of nitrogen. Fourier Transform Infrared Spectroscopy (FTIR) was performed on KBr pellets in the range of 4000 to 400 cm\textsuperscript{-1} using Perkin-Elmer Spectroscopy. Elemental analyses (C, H, O, and N) were carried out by Elementar Vario MICRO elemental analyzer. Powder X-ray diffraction (PXRD) parameters were obtained using a Rigaku-DMAX 2500 diffractometer at a scan rate of 5\textdegree{} min\textsuperscript{-1} from 10\textdegree{} to 70\textdegree{}. Scanning electron microscopy (SEM) experiments were executed on a JSM 6700 at 10.0 kV. Transmission electron microscopies (TEM) and High resolution TEM were conducted on a FEI model Tecnai 20 microscope and a JEOL model JSM-2100F. The samples used in the SEM and TEM tests were fabricated by drop-casting a super sonicated ethanol suspension of POPs onto a copper grid. The calculated specific surface areas for N\textsubscript{2} were based on the BET model over a relative pressure (P/P\textsubscript{0}) between 0.05 and 0.15. Pore size distributions curves were obtained from the adsorption isotherms by the non-local density
functional theory (NLDFT). Total pore volumes were calculated from the uptake curves at a relative pressure of 0.995. Raman spectrum was examined on a LabRAM HR at the range from the 0 to 4000 cm\(^{-1}\). X-ray Photoelectron Spectroscopy was conducted on XPSESCALAB 250Xi analyser. \(^1\)H NMR spectra were recorded using an Avance Bruker DPX 400 (400 MHz) in the solvent of CDCl\(_3\). Solid-state \(^1\)H-\(^{13}\)C CP/MAS NMR were collected on Bruker Bruker-BioSpin Avance III 400 MHz spectrometer.

**Section 2. Synthetic Procedures**

All chemicals including hexachlorocyclotriphosphazene (HCCP), phenol, and p-hydroxy benzaldehyde tetrahydrofuran (THF), triethylamine (TEA) and sodium hydroxide (NaOH) were obtained from commercial source. And all these reagents were used directly without further purification.

**Synthesis of hexaphenoxycyclotriphosphazene (HCTP)**

![Chemical reaction diagram](image)

To a 500mL three-neck round bottom flask equipped with mechanical stirring and reflux condensation, sodium hydroxide (13.2 g, 0.33 mol) and phenol (2, 30.0 g, 0.32 mol) were added. After degas for several times, THF (200 mL) was injected into the reaction system. Then the system
was degassed again and protected under the protection of argon. The mixture was stirred for half an hour, obtaining a suspension of sodium phenate. Subsequently, hexachlorocyclotriphospha
gene (1, 13.92 g, 0.04 mol) that pre-dissolved in 100 ml THF was added dropwise to the flask for more than 1 h under continuous stirring. Then reaction was heated to reflux for 12 h under the atmosphere of Ar. After that, the solvent was separated by reduced pressure via rotary evaporators. The remaining solid product was washed with hot deionized water repeatedly and finally recrystallized from THF to give the resulting product HCTP (22.7 g, yield~80%). White solid, m.p. 110-113°C; IR, $\nu_{\text{max}}$ (cm$^{-1}$): 1486 (Ph), 1197 (-P=N-), 952 (P-O); $^1$H-NMR: $\delta$ 7.18-6.85 (Ar-H).

**Synthesis of hexa-(4-aldehyde-phenoxy)-cyclotriphospha
gene (HACTP)$^{82}$**

4-hydroxybenzaldehyde (35 g, 0.28 mol) was added into a 500ml three-neck round bottom equipped with a mechanical stirrer and a reflux condenser, following by the injection of 150 mL THF. Then TEA (28 g, 0.28 mol) was added into the reaction system as the acid scavenger agent.
The reaction system was protected under the atmosphere of argon. Afterwards, HCCP (1, 14 g, 0.04 mol) that was pre-dissolved in 50 mL THF was added dropwise into the flask continuously and slowly at room temperature. Then, the reaction system was heated slowly to reflux and kept for 24 h. After that, the reaction mixture was filtered to remove the generated triethylamine hydrochloride for twice. The solution was concentrated on a rotary evaporator. Then a large amount of water was poured into to the flask to precipitate the crude product. The crude product was purified initially by filtration to obtain the crude solid. The obtained crude compound HACTP was recrystallized and purified by ethyl acetates. White solid was obtained (30.6 g, yield~90 %). $^1$H NMR (CDCl₃): 9.9 (6H, -CHO) and 7.13-7.75 ppm (24H, -C₆H₄).

**Preparation of PNK-CMP**

PNK-CMP is synthesized via the copolymerization of 2,2'-(1,4-phenylene)diacetonitrile and HCTP referred to Knoevenagel reaction under the catalytic of sodium methoxide in methyl alcohol/THF mixtures. In brief, to a 1000 mL dry three-necked flask equipped with a mechanical agitation, hexakis (4-acetylphenoxy) cyclotriphosphazene (HACTP, 15 g, 0.0174 mol) and 500 mL of tetrahydrofuran (THF) were added in sequence and under nitrogen protection. After the completely dissolving of HACTP, terephthalonitrile (8.1 g, 0.0519 mol) and sodium methoxide (5.6 g, 0.10 mol) were added. The reaction system was
refluxed for 48 h. Then it was cooled to room temperature and treated through washing and vacuum filtering, obtaining a yellow powder. Subsequently, it was purified by Soxhlet extraction in the mixed solvent of CHCl₃ and Methanol. After that, it was transferred to a vacuum oven dried at 50 °C for 5 h and get the final products. Elemental analysis (wt%): C 58.815, H 3.600, N 7.759.

**Synthesis of PNS-CMP**

PNS-CMP was also prepared according to the previous reported protocols. PNS-CMP was fabricated via the self-polymerization of hexanoxy cyclotriphosphonitrile (HCTP) according to Scholl reaction under the catalytic of AlCl₃ in chloroform. In brief, under the protection of nitrogen, hexaphenoxycyclotriphosphazene (HCTP, 0.0072 mol) and 200 mL of dichloromethane were sequentially added to a 5 L dry three-necked flask. After it was completely dissolved, aluminum trichloride (AlCl₃, 20 g, 0.15 mol) was added in three times, and the reaction was refluxed for 72 h. Then it was cooled to room temperature, suction-filtered to obtain a brown solid, the filter cake was rinsed with ethanol, washed with 30 ml of dilute hydrochloric acid and water (1: 1), filtered, washed with ethanol again to obtain a brown powder, and then subjected to Soxhlet extraction until the solution has no change in color, it is transferred to a 50 °C vacuum drying oven and dried for 5 h obtaining the PNS-CMP as abrown powder. Elemental analysis (wt%): C 62.022, H 4.114, N 5.700.
**Preparation of PNK-800**  
PNK-800 was prepared via simple carbonization of PNK-CMP under the atmosphere of Ar. The detailed procedure is conducted as follows: PNK-CMP was ground finely. Then it was transferred to Nickel crucible. Under the protection of Ar, the mixture was heated to 800 °C with a heating rate of 5 °C min⁻¹. And it kept for 120 mins. After the system was cooled down to the room temperature, it was removed from the tube furnace.

**Preparation of PNS-800**  
PNS-800 was prepared via simple carbonization of PNS-CMP under the atmosphere of Ar. The detailed procedure is conducted as follows: PNS-CMP was ground finely. Then it was transferred to Nickel crucible. Under the protection of Ar, the mixture was heated to 800 °C with a heating rate of 5 °C min⁻¹. And it kept at target temperature for 120 mins. After the system was cooled down to the room temperature, it was removed from the tube furnace.

**Preparation of Hyperporous Carbon (PNKA-800 and PNSA-800)**  
PNKA-800 was prepared via simple carbonization of PNK-CMP with the activation of KOH under the atmosphere of Ar. The detailed procedure is conducted as follows: PNK-CMP was finely mixed with KOH in a weight ratio of \( m_{\text{polymer}} : m_{\text{KOH}} = 1:2 \). The mixture was ground finely. Then it was transferred to Nickel crucible. Under the protection of Ar, the mixture was heated to 800 °C with a heating rate of 5 °C min⁻¹. And it kept at target temperature for 120 mins.
temperature for 120 mins. After the system was cooled down to the room temperature, it was removed from the tube furnace. The obtained crude product was washed with HCl (3M) until the filtrate was neutral. Then it was dried under vacuum at 80 °C.

PNSA-800 was prepared identical to the way for the preparation of PNKA-800.

Schematic S1. ¹H NMR, ¹³C NMR and ³¹P NMR of prepared monomers. a) ¹³C NMR of HACTP; b) ¹³C NMR of HCTP; c) ¹H NMR of HACTP; d) ¹H NMR of HACTP; e) ³¹P NMR of HACTP; f) ¹H ³¹P NMR of HACTP.
Electrochemical Measurements\textsuperscript{S3-S8}

All electrochemical tests were recorded via a standard three-compartment cell at ambient temperature. The counter electrode was a platinum net and the reference electrode was a Ag/AgCl electrode saturated with KCl. All the potentials were referenced to the reversible hydrogen electrode (RHE) scale according to the Nernst equation \( \left( E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \times \text{pH} + 0.197 \, \text{V}, \text{ at } 25^\circ\text{C} \right) \). The working electrodes is either a rotating disc electrode (RDE) composed of a glassy carbon disc (5.0 mm diameter) or a rotating ring disc electrode (RRDE) constructed by a glassy carbon disc (3 mm diameter) surrounded by an outer Pt-ring (with an inner-diameter of 5 mm and outer-diameter of 7 mm). The catalyst inks were loading on the surface of work electrode. The catalyst inks and the commercial Pt/C (20 wt\%) inks were fabricated by dispersing 5.0 mg catalyst or commercial Pt/C (20 wt\%) into 500 mL mixed solvent (50 $\mu$L Nafion solution (5 wt\%), 300 $\mu$L H\textsubscript{2}O and 150 $\mu$L ethanol) under an ultrasonic bath to get an even suspensions. Then 8 $\mu$L catalyst ink was pipetted onto the glassy carbon surface of the RDE or the RRDE and leave it to dry in air at room temperature.

The catalytic activities were estimated by cyclic voltammetry (CV), rotating ring-disk electrode (RRDE) and rotating disk electrode (RDE) measurements technique via a three-electrode cell system on a CHI-760 electrochemical workstation. All the tests are performed in alkaline
conditions (0.1 M KOH) saturated with O\textsubscript{2} or Ar. The CV measurements were carried out with a scan rate of 50 mV s\textsuperscript{-1} and the RDE/RRDE experiments were examined with a scan rate of 5 mV s\textsuperscript{-1} with different rotating speeds from 400 to 2500 rpm. For comparison, the catalytic performance of commercial Pt/C was also tested under identical conditions. The Koutecky-Levich (K-L) plots were analyzed at various electrode potentials. The slopes of their best linear fit lines were used to calculate the electron transfer numbers (n) according to K-L equations \textsuperscript{(1)}\textsuperscript{53} - \textsuperscript{(2)}\textsuperscript{54}:

\[
\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K} \quad (1)
\]

In this equation, \(J_L\) is the current that was measured; JK represents the kinetic-limiting current and \(\omega\) is the rotation speeds of electrode.\textsuperscript{55}

\[
B = 0.62 nFC_0(D_0)^{2/3}V^{1/6} \quad (2)
\]

In equation 2, \(n\) is the total number of transferred electrons during the oxygen reduction process; F is Faradaic constant (F = 96485 C mol\textsuperscript{-1}), \(C_0\) is the O\textsubscript{2} concentration (solubility) in 0.1 M KOH electrolyte (1.2 \times 10\textsuperscript{-6} mol cm\textsuperscript{-3}); \(D_0\) is the O\textsubscript{2} diffusion coefficient (1.90 \times 10\textsuperscript{-5} cm\textsuperscript{2} s\textsuperscript{-1}) and V is the kinematic viscosity of the O\textsubscript{2} saturated 0.1 M KOH solution (0.01 cm\textsuperscript{2} s\textsuperscript{-1}).

For the RRDE measurements, the disk electrode was also scanned with a rate of 5 mV s\textsuperscript{-1} at a constant ring potential of 1.5 V vs. RHE. The peroxide percentage (H\textsubscript{2}O\textsubscript{2} yields) and the transferred number of electron
(n) were calculated according to the following equations (3) - (4):\(^{6,7,8}\)

\[
H_2O_2\% = 200 \times \frac{I_r/N}{I_d+I_r/N} \quad (3)
\]

\[
N = 4 \times \frac{I_d}{I_d+I_r/N} \quad (4)
\]

In equation 3 and 4, \(I_d\) is the disk current, and \(I_r\) refers to the ring current and \(N\) represents the current collection efficiency of the Pt ring (\(N=0.4581\)).

**Section 3. FT-IR Spectra**

![FTIR Spectra](image)

**Figure. S1** FTIR spectra of monomers and prepared polymers. a) FTIR of HACTP; b) FTIR of HCTP; c) FTIR of PNK-CMP; d) FTIR of PNS-CMP; e) FTIR of cyclotriphosphazene based porous organic polymers: Black line is the PNK-CMP prepared by the Knoevenagel reaction; red line represents the PNS-CMP synthesized by Scholl polymerization reaction.
Section 4. $^{13}$C and $^{31}$P Solid-state NMR

![Graphs showing $^{13}$C and $^{31}$P NMR spectra for CP-based CMPs.]

**Figure S2.** Solid-state $^{13}$C and $^{31}$P NMR for the CP based CMPs. a) Solid-state $^{13}$C NMR of PNK-CMP; b) Solid-state $^{31}$P NMR of PNK-CMP; c) Solid-state $^{13}$C NMR of PNS-CMP.

Section 5. SEM & TEM Images

![Images of SEM and TEM of PNKA-800 and PNSA-800.]

**Figure S3.** SEM and TEM of PNKA-800 and PNSA-800. a) SEM of PNKA-800 at a scale bar of 1 um; b) HR-TEM of PNKA-800 at a scale bar of 10 nm; c) SEM of PNSA-800 at a scale bar of 500 nm; b) HR-TEM of PNKS-800 at a scale bar of 5 nm.
Section 5. PXRD Profiles

Figure S4. a) PXRD Profiles of cyclotriphosphazene based Conjugated Microporous Polymers, black line is the PNK-CMP prepared by the Knoevenagel reaction; red line represents the PNS-CMP synthesized by Scholl polymerization reaction; b) PXRD Profiles of polymers derived hyper porous carbon (PNKA-800 and PNSA-800), red line is the hyperporous carbon (PNKA-800) prepared via the carbonization of PNK-CMP with the activation of KOH at 800°C and the blue line represents hyperporous carbon (PNSA-800) with the activation of KOH using PNS-CMP as precursors at 800°C.

Section 7. Thermogravimetric Analysis (TGA)

Figure S5. TG of prepared cyclotriphosphazene based monomers and porous polymers. a) TG of HCTP; b) TG of HACTP; c) TG of PNS-CMP; d) TG of PNK-CMP.
Section 8. Raman Spectra

Figure S6. Raman spectrum of prepared hyperporous carbon.

Section 8. X-ray Photoelectron Spectra (XPS)

Figure S7. XPS of PNSA-800. a) Survey spectrum of PNSA-800; b) High-resolution XPS C 1s of PNSA-800; c) N 1s spectrum of PNSA-800; d) High-resolution XPS P 2p of PNSA-800; e) spectrum O 1s of PNSA-800.
Section 9. Electrocatalytic performance

![Graphs showing electrocatalytic performance](image)

**Figure S8.** Electrocatalytic performance of control materials. a) CV curves of commercial Pt/C in 0.1 M KOH saturated with O₂ or argon at a sweep rate of 50 mV s⁻¹; b) LSV of commercial Pt/C at various rotation speeds; c) K-L plots curves of commercial Pt/C (20%); d) Percentage of hydrogen peroxide yield and the electron transfer number (n) of Pt/Cat different potentials; e) Ring and disk current measured by RRDE electrode; f) LSV curve of Pt/C measured before and after the injection of 3 M methanol.

Section 10. TGA of Composites

![Graphs showing TGA of composites](image)

**Figure S9.** TG of prepared fabricated composites. a) TG of POP/TPU composites in a mass ratio of 10% : 90%; b) TG of PEPA/POP/TPU composites in a mass ratio of 5% : 5%: 90%; c) TG PEPA/TPU composites in a mass ratio of 10%: 90%.
Section 11. Supporting Tables

Table S1. Porosity Parameters of prepared polymers and corresponding catalysts.

| sample   | $S_{BET}$ (m$^2$/g) | $S_{Langmuir}$ (m$^2$/g) | $S_{Micro}$ (m$^2$/g) | $V_{Micro}$ (cm$^3$/g) | $V_{Total}$ (cm$^3$/g) | Main pore size (nm) |
|----------|----------------------|---------------------------|------------------------|------------------------|------------------------|---------------------|
| PNK-CMP  | 138                  | 838                       | 594                    | 0.209                  | 0.272                  | 2.18/1.60/2.74/3.79 |
| PNS-CMP  | 173                  | 695                       | 508                    | 0.221                  | 0.287                  | 0.55/1.43/2.67      |
| PNK-800  | 513                  | 524                       | 592                    | 0.408                  | 0.44                   | 0.60/1.60/2.78      |
| PNS-800  | 479                  | 702                       | 707                    | 0.39                   | 0.42                   | 0.54/1.17/3.79      |
| PNKA-800 | 3001                 | 691                       | 773                    | 0.89                   | 1.371                  | 0.57                |
| PNSA-800 | 1812                 | 598                       | 510                    | 0.77                   | 1.182                  | 1.43                |

Table S2. Main parameters of the PNKA-800 and commercial Pt/C catalysts in alkaline conditions

| Sample  | On-set Potential ($E_{onset}$, V) | Half-wave potential ($E_{1/2}$, V) | Current density (mA cm$^{-2}$; at 0.5V) | Electron transfer number (n, at 0.2 V) |
|---------|-----------------------------------|------------------------------------|------------------------------------------|---------------------------------------|
| PNKA-800| 0.935                             | 0.756                              | 4.47                                     | 3.64                                  |
| Pt/C (20%) | 0.101                           | 0.845                              | 5.60                                     | 3.99                                  |