

Electronic supplementary information (ESI)

Intumescent flame retardant-derived P,N co-doped porous carbon as an efficient electrocatalyst for the oxygen reduction reaction

Yinling Wang,^{*a} Xuemei Zhang,^a Anna Li^a and Maoguo Li^{*a}

Experimental section

Chemicals. Dopamine hydrochloride (DA) was purchased from Acros Organics (New Jersey, USA). Melamine (MA) was of chemical pure, purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd (Shanghai, China). Ammonium polyphosphate (APP) was kindly provided by Professor Hu and Dr. Song from State key laboratory of fire science of University of Science and Technology of China (USTC, Hefei, China). 20% Pt/C was purchased from Alfa Aesar (Johnson Matthey Public Limited Company, England). All the reagents were used without further purification. Milli-Q purified water (Millipore, ≥ 18.2 M Ω cm) was used throughout the study.

Synthesis of C-PMA, C-P, C-PM and C-PA. For preparation of C-PMA, 1 g DA, 25 g MA and 150 mg APP were dispersed in 100 mL ultrapure water. Then the pH value was adjusted to 8.5 using Tris buffer solution and stirred for 24 h for the polymerization of DA. After washed by ultrapure water and ethanol, the precipitation was dried at 60 °C. Finally, the mixture was subjected to a pyrolysis at 1000 °C for 1 h with the protection of high purity nitrogen. The synthesis of C-P, C-PM and C-PA were similar to that of C-PMA.

Material characterization. X-ray diffraction (XRD) patterns were recorded by a D8 advance diffractometer (Gernamy, Bruker). Scanning electron microscopy (SEM) images were obtained from a JEOL JSM-6700F field emission scanning electron microscope (FE-SEM); Transmission electron microscopy (TEM) studies of the carbon materials were carried out on a TECNAI-G2 F20 microscope (FEI, US). X-ray photoelectron spectroscopy (XPS) was performed using a Thermo ESCALAB 250XI spectrometer with Al K α radiation (Thermo Fisher

Scientific, USA). The Brunauer-Emmet-Teller (BET) tests of the samples were measured by N₂ adsorption/desorption using a 3Flex adsorption instrument (US, Micromeritics). Raman spectra were tested on a LabRAM HR800 confocal microscope Raman system (Horiba Jobin Yvon).

Preparation of modified electrodes. Prior to use, the GCE was carefully polished with alumina powder (1.0, 0.3, 0.05 μm orderly) on a wet polishing cloth and then thoroughly cleaned ultrasonically in acetone and pure water. Next, for CV and chronoamperometry measurement, 5 μL of the suspension of catalyst (5 mg/mL, dispersed in water by ultrasonication) were casted on the GCE (the loading amount of catalyst is about 0.352 mg cm^{-2}) and was later covered with a layer of Nafion film. For RDE measurements, 10 μL of the suspension were dropped onto the GC disk work electrode (the loading amount of catalyst is about 0.255 mg cm^{-2}), which was also immobilized by a layer of Nafion film.

Electrochemical measurements. Cyclic voltammetry (CV) and chronoamperometry were carried out on a CHI660C electrochemical workstation (CH Instruments, Shanghai, China). A conventional three-electrode system was employed with a platinum wire as the counter electrode, an HgO/Hg (0.1 M KOH) electrode as the reference electrode, and a modified glassy carbon electrode (GCE, 3 mm in diameter) as the working electrode.

The rotating disk electrode (RDE) measurements were performed on a Bipotentiostat Model AFCBP1 electrochemical workstation with a mating rotating disk electrode (RDE, Pine Research Ins, USA). A similar three-electrode system to that of cyclic voltammetry was adopted except that the GC disk electrode was 5 mm in diameter.

All the electrochemical measurements were conducted in 0.1 M KOH saturated with N₂ or O₂. The scan rates are 50 mV s^{-1} for CV and 10 mV s^{-1} for RDE measurements, respectively.

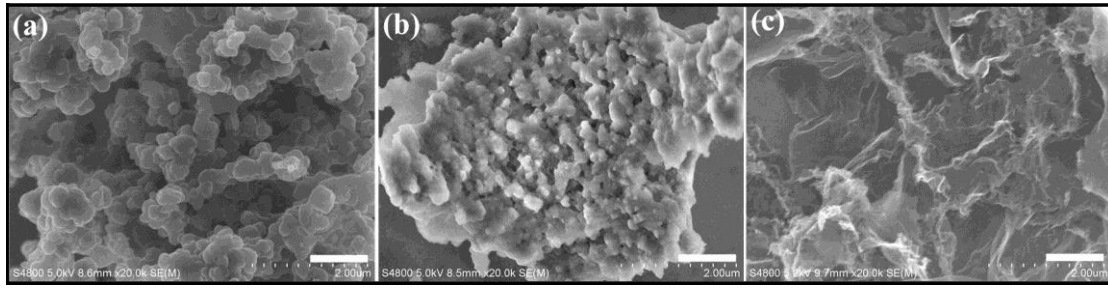


Fig. S1 SEM images of (a) C-P, (b) C-PA, and (c) C-PM. The scale bar is 1 μm .

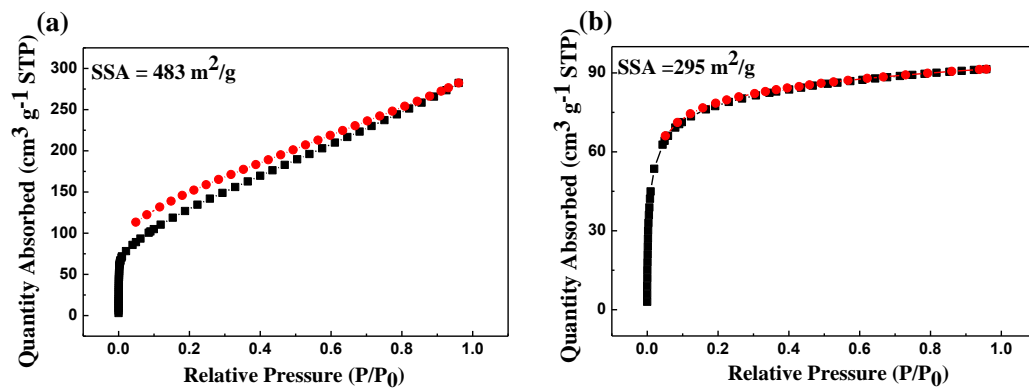


Fig. S2 N_2 adsorption-desorption isotherm of (a) C-P and (b) C-PM.

Table S1 Composition of the specific surface area for different carbon materials.

Material	S_{BET} (m^2/g)	S_{micro} (m^2/g)	S_{external} (m^2/g)
C-P	483	Negative value	535
C-PM	296	163	133
C-PMA	401	296	170

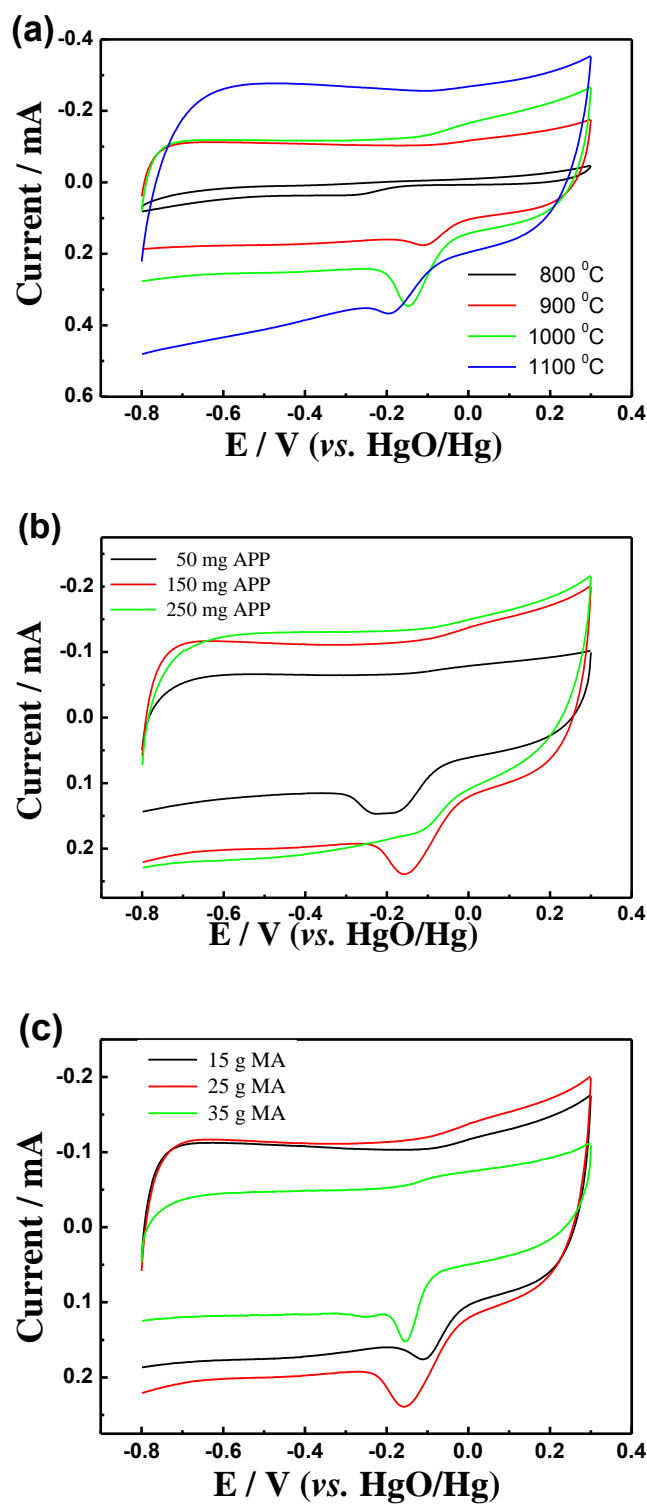


Fig. S3 CV curves of (a) C-MPA prepared at different temperature, (b) C-MPA prepared at 1000 $^{\circ}\text{C}$ with different mass of APP (The mass of DA was fixed at 1 g and The mass of MA was fixed at 25 g), and (c) C-MPA prepared at 1000 $^{\circ}\text{C}$ with different mass of MA (The mass of DA was fixed at 1 g and The mass of APP was fixed at 150 mg) in the O_2 -saturated 0.1 M KOH solution at a scan rate of 50 mV s^{-1} .

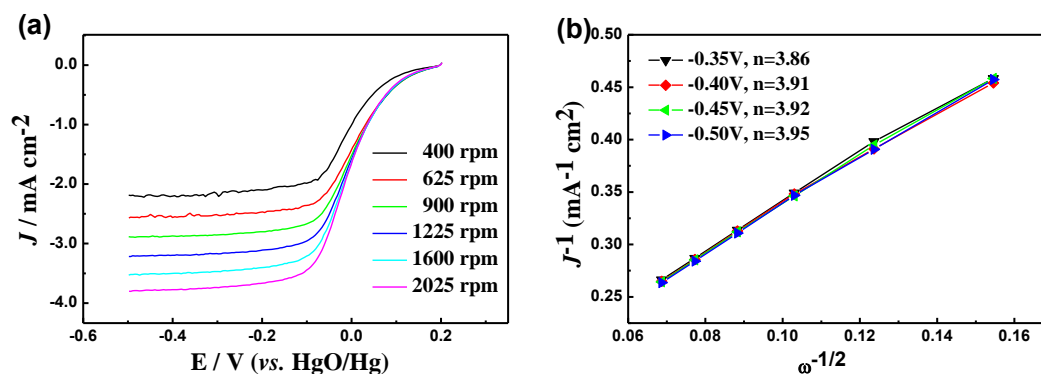


Fig. S4 (a) LSV curves at different rotation rates of 20% Pt/C and (b) the corresponding Koutecky-Levich plots (J^{-1} versus $\omega^{-1/2}$) at different electrode potentials. The average transferred electron number is about 3.9.

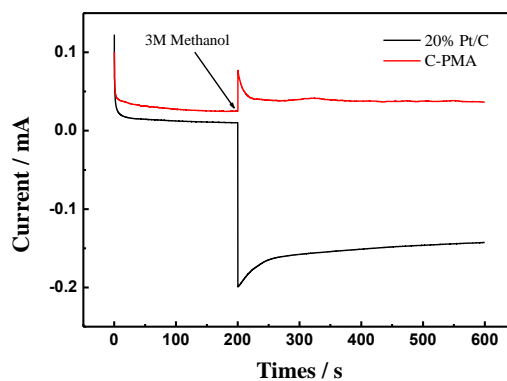


Fig. S5 The effect of methanol on the chronoamperometric responses of C-PMA and 20% Pt/C in O₂ saturated 0.1 M KOH solution. The applied potential is fixed at -0.3V.