Electronic Supporting Information (ESI†)

From Filter Paper to Porous Carbon Composite Membrane Oxygen Reduction Catalyst

Wenxiu Yang, Yanling Zhai, Xiaoyu Yue, Yizhe Wang, Jianbo Jia*

State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry,

University of Chinese Academy of Sciences, Beijing 100049, P. R. China

Chinese Academy of Sciences, Changchun, Jilin 130022, P. R. China

Preparation of the PCCM

Filter paper was bought from Hangzhou Xinhua paper (Hangzhou, China). Pt catalyst (20 wt %, Pt/C) was bought from Johnson Matthey. Nafion (5.0 wt %) were purchased from Sigma–Aldrich. Iron nitrate, and methanol were bought from Beijing Chemical Reagent Company (Beijing, China). All the chemicals were analytical grade, and used as received. All aqueous solutions were prepared with ultrapure water from a Water Purifier System (Sichuan Water Purifier Co. Ltd., China).

The commercial filter paper was stabilized at 240 °C for 2 h in a muffle at a heating rate of 2 °C/min. Then the material was impregnated with a selected concentration of $Fe(NO_3)_3$, for example, 4.0, 3.0, 2.0, 1.0, 0.5, or 0 wt %, dried it at room temperature. Finally, the catalyst was prepared by temperature-programming in a tube furnace under N_2 at a heating rate of 2 °C/min, for simplicity, that is, the mixture was heated at 180, 240, and 900 °C for 2, 2, and 1 h, respectively. The final product was named as $PCCM_{900}$-1% based on the pyrolysis temperature (900 °C) and concentration of $Fe(NO_3)_3$ (1.0%), respectively. To explore the ORR active sites of the PCCM catalyst, the $PCCM_{900}$-1% was grinded by the agate mortar and pestle for 40 min, leached by 0.5 M H_2SO_4 at 85°C for 6 h, and followed by drying at 80°C. The resulting sample was named as g-$PCCM_{900}$-1%.

With an accelerating voltage of 20 kV scanning electron microscopy (SEM) images and

EDAX (Genesis 2000) were obtained from an XL 30 ESEM FEG SEM (Philips, Netherlands). Transmission electron microscopy (TEM) measurements were made on a HITACHI H-8100 EM with an accelerating voltage of 100 kV. High resolution TEM images were obtained with a JEM-2100F high-resolution transmission electron microscope operating at 200 kV. BET surface areas and Nitrogen sorption isotherms were measured with an ASAP 2020 Physisorption Analyzer (Micrometrics Instrument Corporation). X-Ray diffraction (XRD) data were obtained with model D8 ADVANCE (BRUKER, Cu K_α radiation, □ =1.5406 Å). X-Ray photoelectron spectroscopy (XPS) analysis was got on an ESCALABMKII X-ray photoelectron spectrometer (VG Scientific, UK). TGA was performed with NETZSCH STA 449F3.

Electrochemical Tests

All the measurements were carried out at room temperature. The electrochemical experiments were performed using a CHI842B electrochemical workstation (CH Instruments, Shanghai). Rotating ring-disk electrode (RRDE) techniques were employed on a Model RRDE-3A Apparatus (ALS, Japan) with a CHI842B electrochemical workstation. The electrochemical experiments were carried out via a three electrode cell with a modified glassy carbon electrode (GCE, □ = 3.0 mm) as the working electrode, an Ag/AgCl (saturated KCl) electrode as the reference electrode, and a platinum foil as the counter electrode, respectively.

Before modification, the GCE was polished carefully with 0.3 μm alumina slurries, followed by sonication in acetone, ethanol and ultrapure water successively, and then was dried at room temperature. For a typical procedure, 4.0 mg of the $PCCM_{900}$-1% sample or Pt catalyst were dissolved in a mixture (4 ml) of water, isopropyl alcohol, and Nafion (5.0 wt %) with a ratio of 20:1:0.75 (v/v/v) under sonication. For the electrochemical measurements, a certain amount of the $PCCM_{900}$-1% suspension was coated onto the pretreated GCE surface (600 μg/cm^2), and then the $PCCM_{900}$-1%/GCE was dried under an infrared lamp before use. For comparison, the Pt/C modified GCE (Pt/C/GCE) was prepared according to the same procedure with suitable amount of catalyst (25 μg Pt/cm^2).

In the RRDE experiments, linear sweeping voltammograms (LSVs) were obtained by performing a negative-direction sweep of potential from 0.2 V at a rate of 5 mV/s, and the ring potential was set at 0.2 V in 0.10 M KOH. Before experiments, all the modified electrodes and the

Pt ring electrode were activated by potential cycling in 0.10 M KOH from 0.2 to −0.8 V at a scan rate of 50 mV/s for 30 cycles.

Characterization of PCCM nanostructures

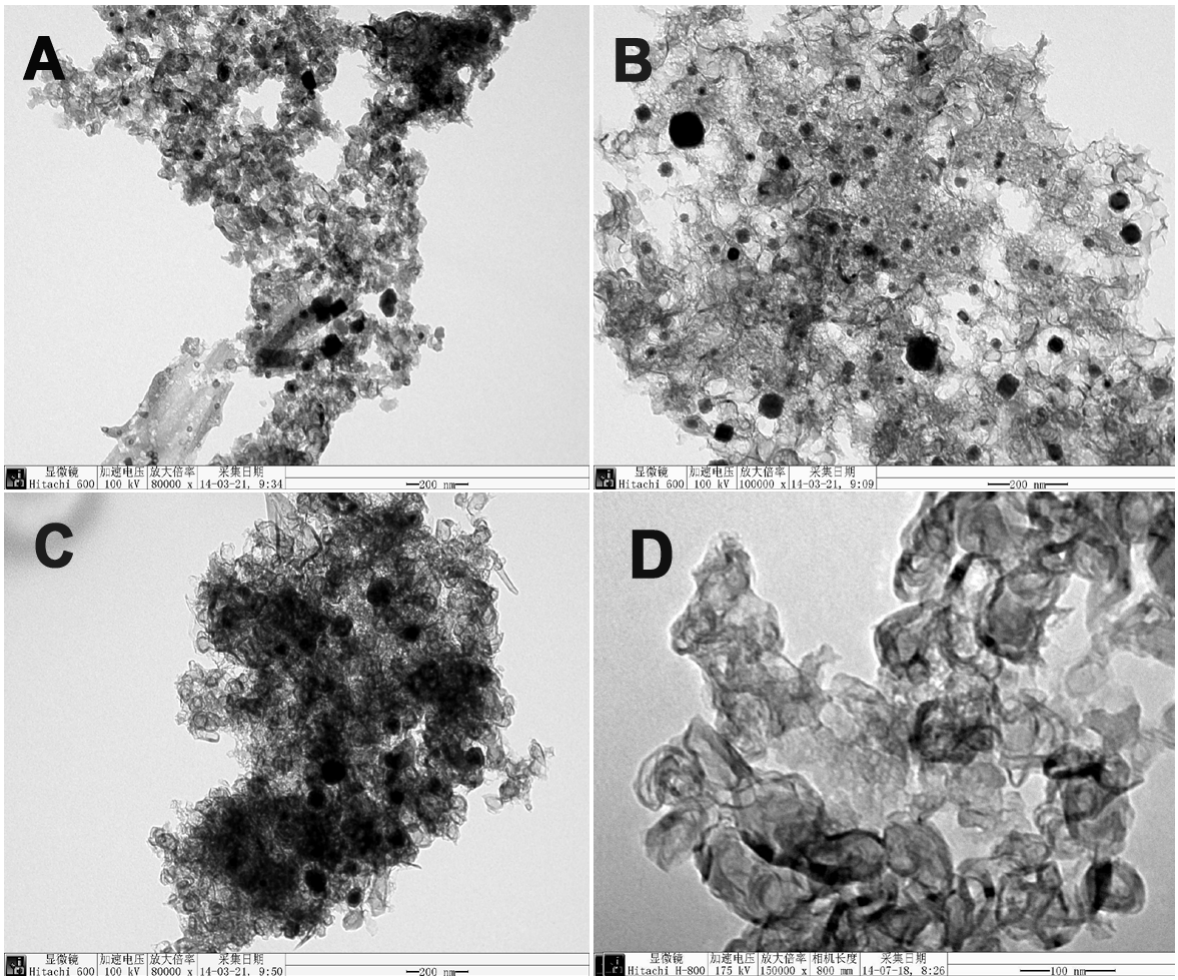

Fig. S1 TEM images of (A) $PCCM_{800}$-1%, (B) $PCCM_{900}$-1%, (C) $PCCM_{1000}$-1%, and (D) g-$PCCM_{900}$-1%.

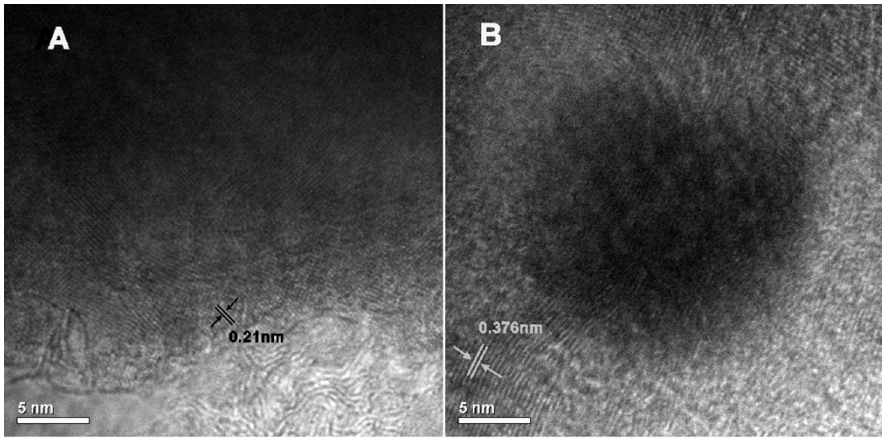

Fig. S2 High resolution TEM images of the $PCCM_{900}$-1%. The distances of 0.21 and 0.376 nm are corresponding to (211) and (011) crystal planes of Fe_3C phase, respectively.

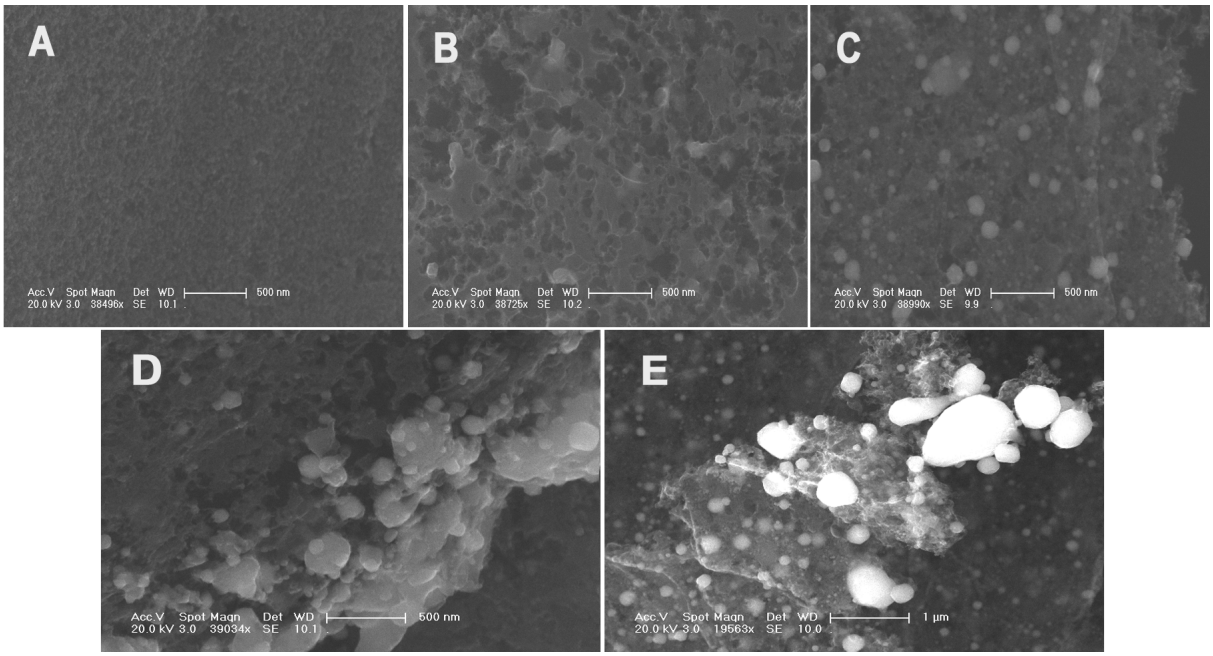

Fig. S3 SEM images of (A) $PCCM_{900}$-0%, (B) $PCCM_{900}$-0.5%, (C) $PCCM_{900}$-1%, (D) $PCCM_{900}$-2%, and (E) $PCCM_{900}$-3%.

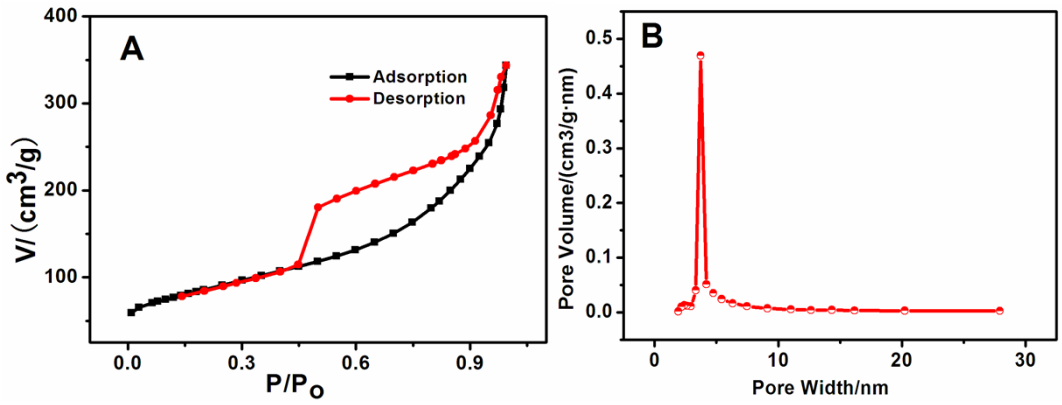

Fig. S4 (A) N_2 adsorption-desorption isotherm of the $PCCM_{900}$-1% composite and (B) the pore size distribution of the composite from BJH plot.

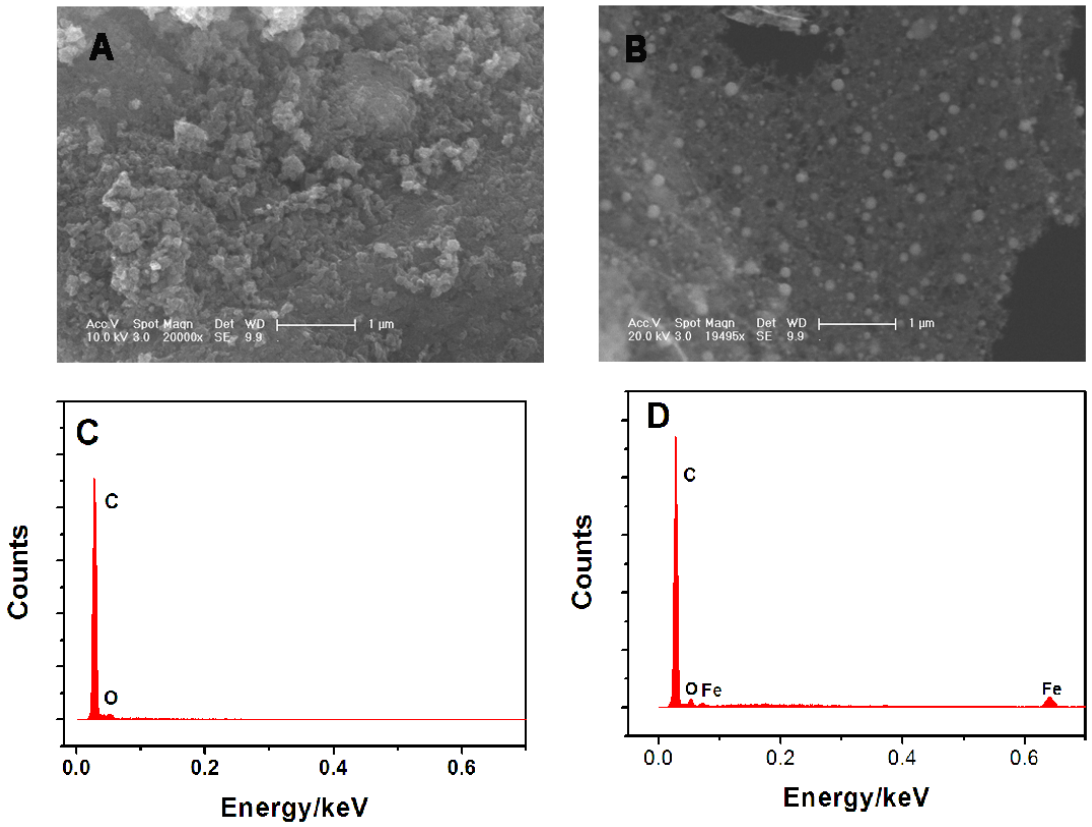

Fig. S5 SEM images of (A) g-PCCM$_{900}$-1%, (B) PCCM$_{900}$-1% and corresponding EDAX spectra of (C) g-PCCM$_{900}$-1% and (D) PCCM$_{900}$-1%.

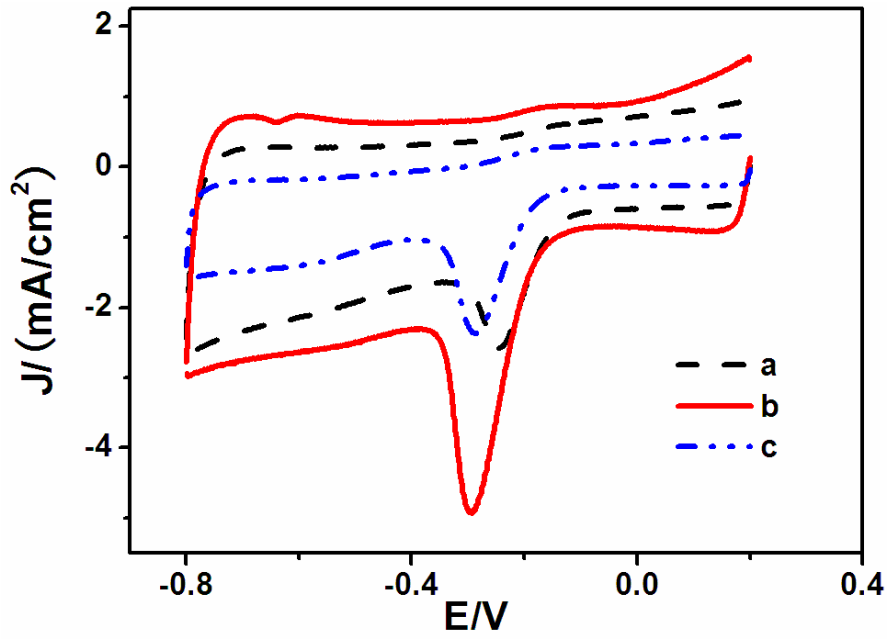

Fig. S6 Cyclic voltammograms (CVs) tested in O_2-saturated 0.10 M KOH: (a) PCCM$_{800}$-1%/GCE, (b) PCCM$_{900}$-1%/GCE, and (c) PCCM$_{1000}$-1%/GCE. Scan rate is 50 mV/s. (vs Ag/AgCl)

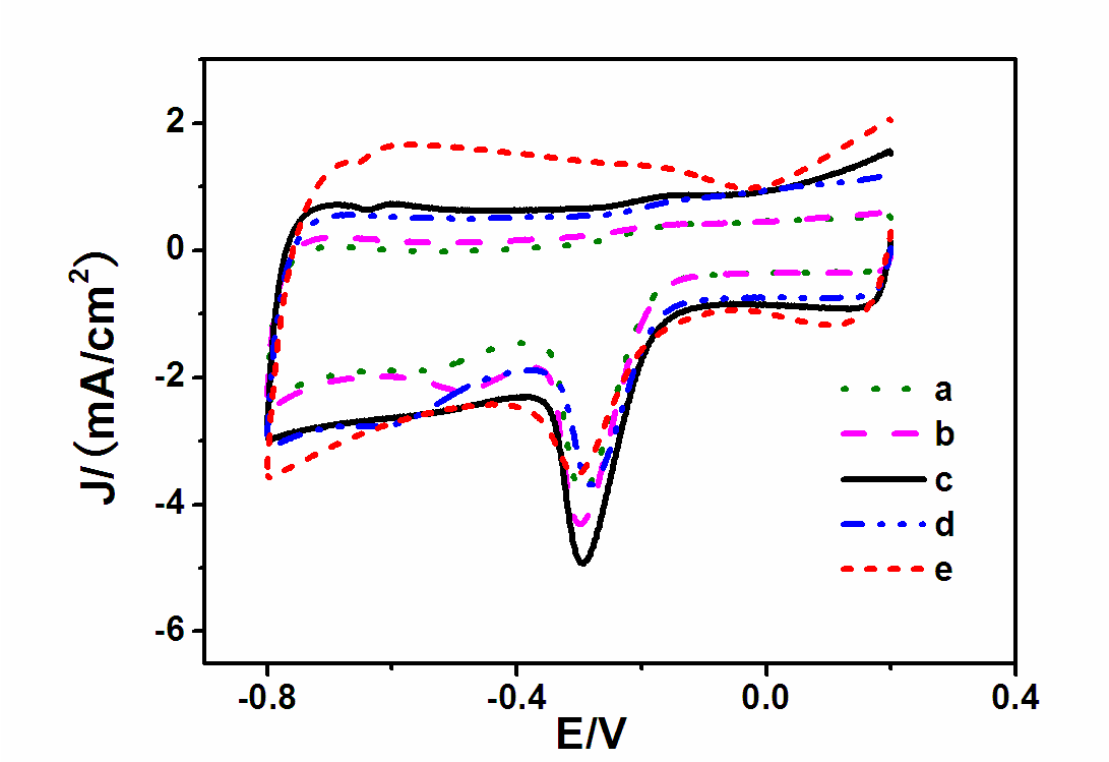

Fig. S7 CVs on different modified GCE in O_2-saturated 0.10 M KOH: (a) $PCCM_{900}$-3%/GCE, (b) $PCCM_{900}$-2%/GCE, (c) $PCCM_{900}$-1%/GCE, (d) $PCCM_{900}$-0.5%/GCE, and (e) $PCCM_{900}$-0%/GCE. Scan rate is 50 mV/s.

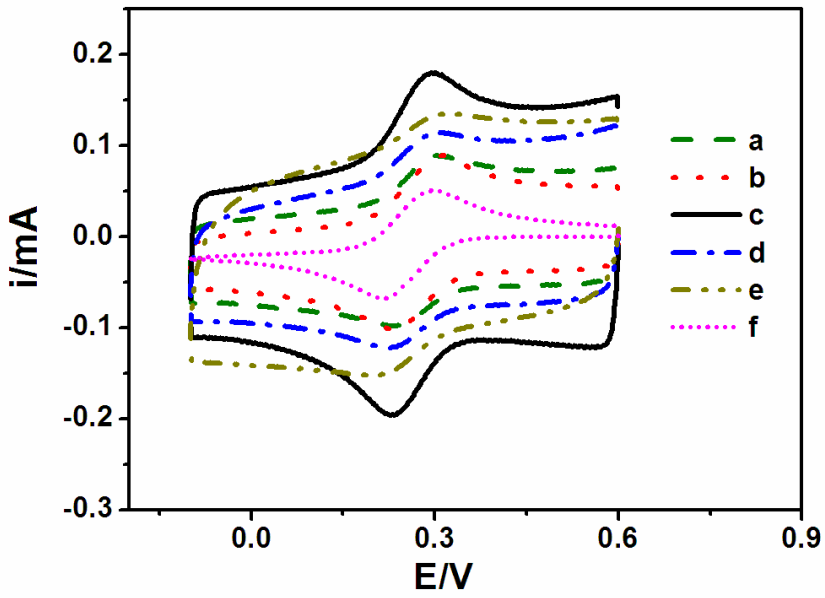

Fig. S8 CVs of different electrodes in 0.50 mM $Fe(CN)_6^{3-}$ containing 1.0 M KCl: (a) $PCCM_{900}$-3%/GCE, (b) $PCCM_{900}$-2%/GCE, (c) $PCCM_{900}$-1%/GCE, (d) $PCCM_{900}$-0.5%/GCE, (e) $PCCM_{900}$-

0%/GCE, and (f) bare GCE. Scan rate is 50 mV/s.

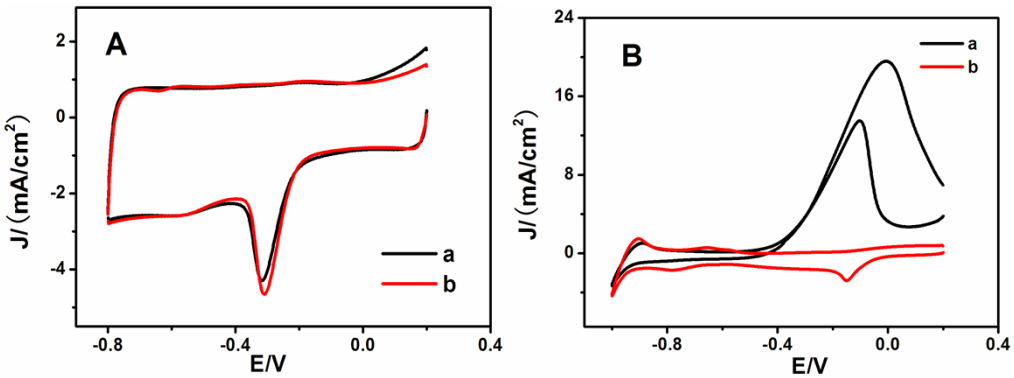

Fig. S9 CVs of (A) $PCCM_{900}$-1%/GCE and (B) Pt/C/GCE in O_2-saturated 0.10 M KOH solution (a) with and (b) without 1.0 M CH_3OH. Scan rate is 50 mV/s.

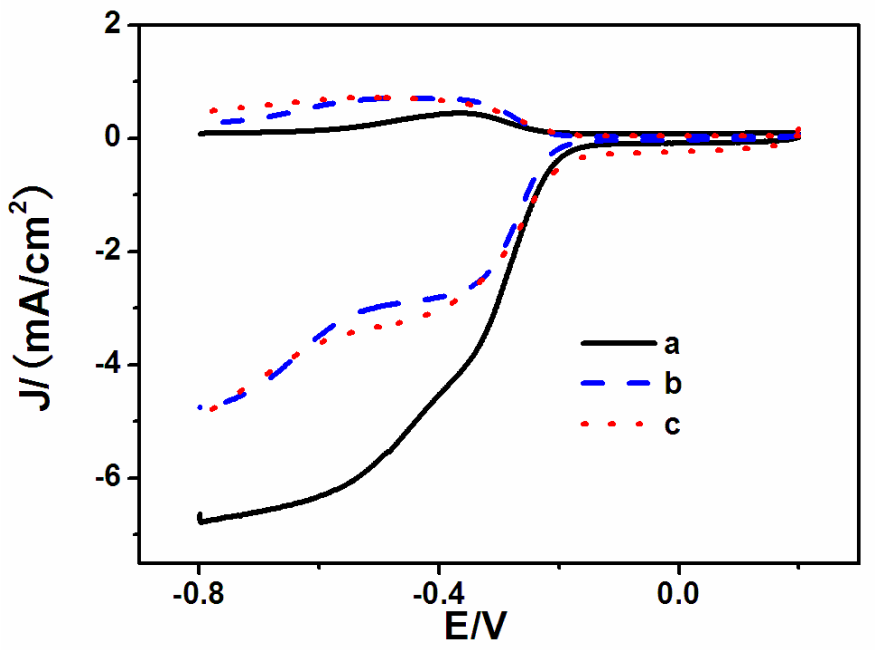

Fig. S10 RRDE voltammograms of (a) $PCCM_{900}$-1%/GCE, (b) g-$PCCM_{900}$-1%/GCE, and (c) $PCCM_{900}$-0%/GCE in O_2-saturated 0.10 M KOH at a scan rate of 5 mV/s, a rotation rate of 1600 rpm, and the Pt ring electrode is polarized at 0.2 V (vs Ag/AgCl).

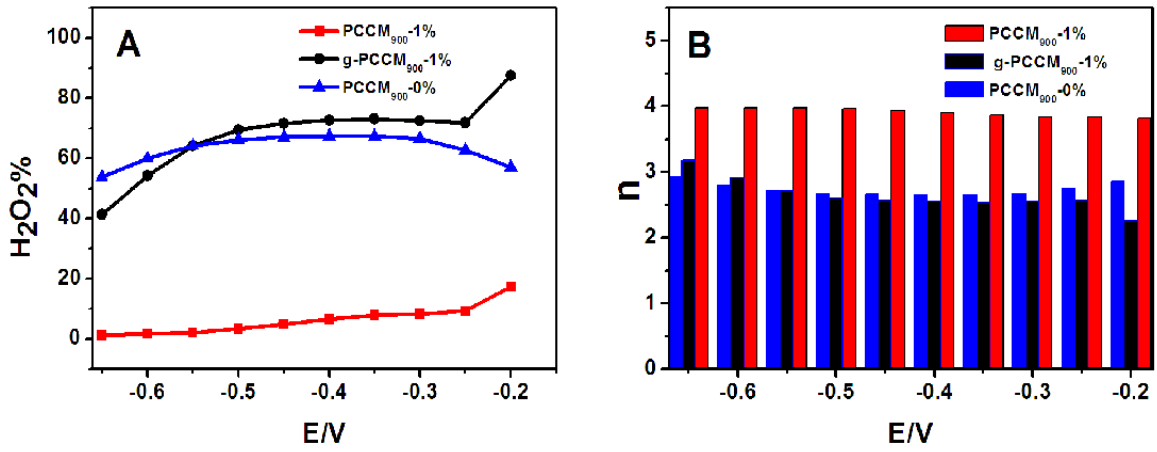

Fig. S11 (A) H_2O_2 yield of the $PCCM_{900}$-1%/GCE, g-$PCCM_{900}$-1%/GCE, and $PCCM_{900}$-0%/GCE. (B) Electron transfer number (n) of the $PCCM_{900}$-1%/GCE, g-$PCCM_{900}$-1%/GCE, and $PCCM_{900}$-0%/GCE.