Electronic Supplementary Material (ESI) for Nanoscale
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Electronic Supplementary Information

Metallated Porphyrin Based Porous Organic Polymers as Efficient Electrocatalysts

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Tables and Figures

Materials and measurements

All reagents and solvents were used as received from commercial suppliers unless otherwise noted. Cobalt (II) 5,10,15,20-tetrakis-(4'-bromophenyl)porphyrin[1] and tetrakis(4-ethynylphenyl)methane[2] were synthesized according to the published procedure.

NMR spectra were taken on Inova 400 and Inova 500 spectrometers. Solid-state cross polarization magic angle spinning (CP/MAS) NMR spectra were recorded on an Inova 400 NMR spectrometer.

The FT-IR spectra of starting materials and as-synthesized CoPOP were obtained from Thermo Nicolet Avatar-370 spectrometer using KBr pellets.

Scanning Electron Microscopy (SEM) images were recorded using a JSM-6480LV (LVSEM) at 5.0 kV. The samples were sputter coated with gold prior to the analysis.

The Quantachrome Autosorb ASiQ automated gas sorption analyzer was used to measure N_2 adsorption isotherms. The samples were activated by heating at 120 °C under vacuum for at least 22 hours prior to the analysis. Ultra high purity grade (99.999 % purity) N_2 and He, oil-free valves and gas regulators were used for all free space corrections and measurements.

Table S1. Loading amount of **CoPOP/C** composites on glassy carbon electrode

Molar loading of Co (mM/cm^2)	**Areal loading of Co (mg/cm^2)**	**Areal loading of CoPOP (mg/cm^2)**	**Areal loading of CoPOP/C (mg/cm^2)**
3.96×10^{-4}	2.33×10^{-2}	0.442	0.78

Table S2. Loading amount of 20 wt% Pt/C catalyst on glassy carbon electrode

Molar loading of Pt (mM/cm^2)	**Areal loading of Pt (mg/cm^2)**	**Areal loading of 20 wt% Pt/C (mg/cm^2)**
1.52×10^{-4}	3×10^{-2}	0.15

Koutecky–Levich (K-L) equations as followings were used to analyze the data from RDE measurements:

$$\frac{1}{j_{Lim}} = \frac{1}{j_{Lev}} + \frac{1}{j_k} \quad (1)$$

$$j_{Lev} = 0.62nFCD^{2/3}\nu^{-1/6}\omega^{1/2} \quad (2)$$

$$j_k = nFkC\Gamma \quad (3)$$

Where, j is the measured current density, ω is the electrode rotation rate, F is the Faraday constant C_0 is the bulk concentration of O_2, D_0 is the diffusion coefficient of O_2, ν is the kinetic viscosity of the electrolyte, and k is the electron-transfer rate constant.

Table S3. Parameters for Koutecky–Levich equations.

Solution	**F (C mol^{-1})**	**C_0 (mol cm^{-3})**	**D_0 (cm^2 s^{-1})**	**ν (cm^2 s^{-1})**
0.5 M H_2SO_4	96485	1.1×10^{-6}	1.4×10^{-5}	0.01
0.1 M KOH	96485	1.2×10^{-6}	1.9×10^{-5}	0.01

The electron transfer numbers (n) were calculated from RRDE measurements based on the disk current (I_{disk}) and ring current (I_{ring}) via the following equation:

$$n = 4\mathrm{I}_{disk}/(\mathrm{I}_{disk} + \mathrm{I}_{ring}/N) \quad (4)$$

where N is current collection efficiency of the Pt ring and equal to 25.6% in our system.

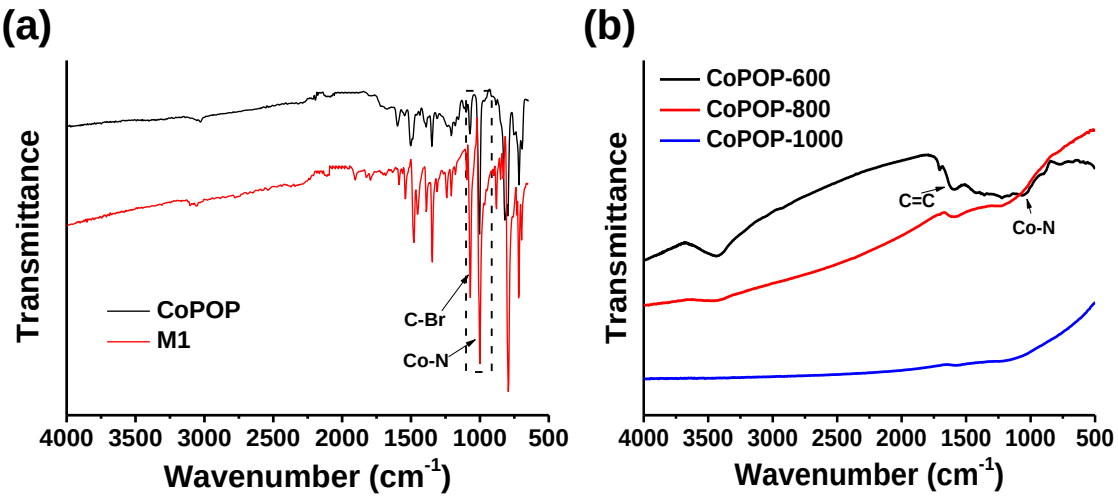

Figure S1. FT-IR spectra of **CoPOP** and **M1** (a), **CoPOP-600**, **CoPOP-800** and **CoPOP-1000** (b).

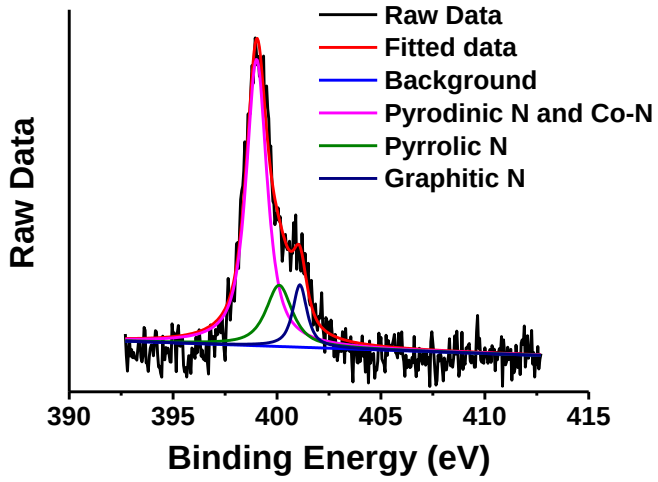

Figure S2. High resolution XPS N1s spectra of **CoPOP-800**.

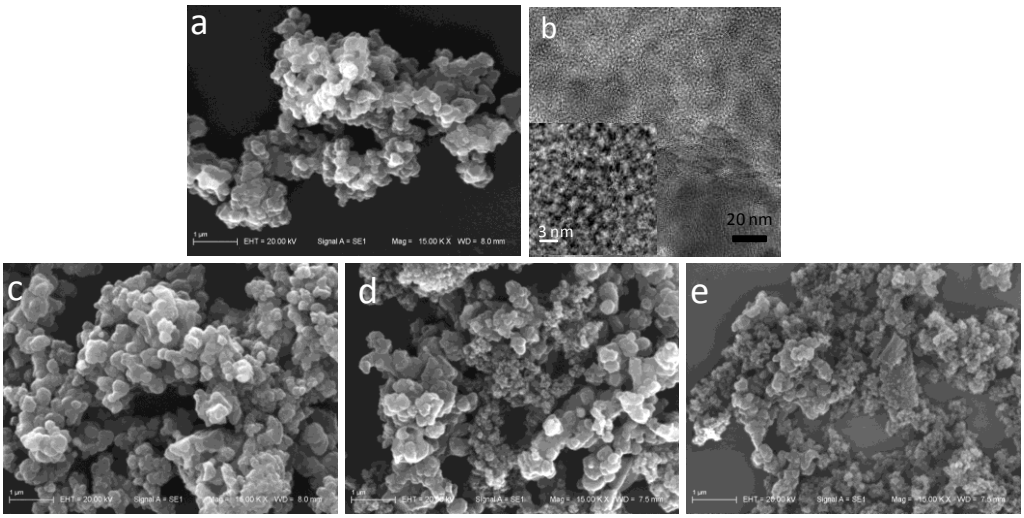

Figure S3. SEM images of **CoPOP** (a), **CoPOP-600** (c), **CoPOP-800** (d), and **CoPOP-1000** (e). HR-TEM image of **CoPOP** (b). The solid samples of **CoPOPs** were used directly for images a, c, d and e.

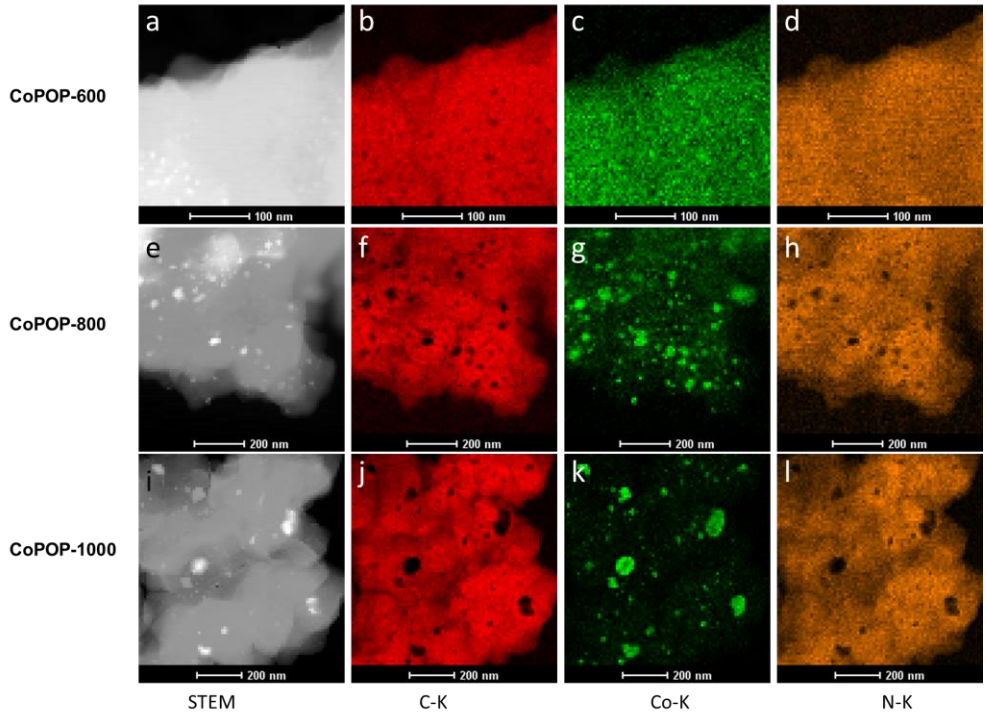

Figure S4. High Angle Annular Dark Field (HAADF) Scanning Transmission Electron Microscopy (STEM) images of **CoPOP-600** (a), **CoPOP-800** (e) and **CoPOP-1000** (i); carbon atom mapping of **CoPOP-600** (b), **CoPOP-800** (f), and **CoPOP-1000** (j); cobalt atom mapping of **CoPOP-600** (c), **CoPOP-800** (g), and **CoPOP-1000** (k); nitrogen atom mapping of **CoPOP-600** (d), **CoPOP-800** (h), and **CoPOP-1000** (i).

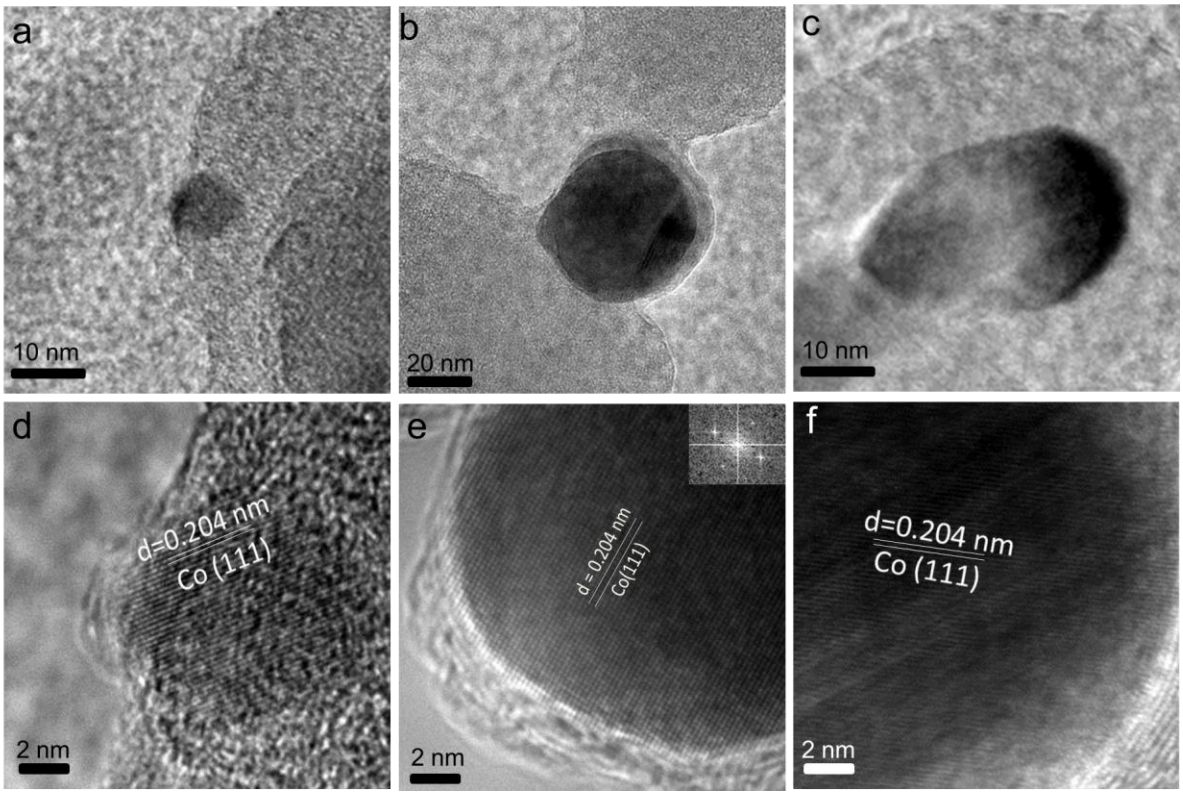

Figure S5. TEM images of **CoPOP-600** (a), **CoPOP-800** (b), and **CoPOP-1000** (c); HRTEM images of a single nanoparticle in **CoPOP-600** (d), **CoPOP-800** (e), and **CoPOP-1000** (f).

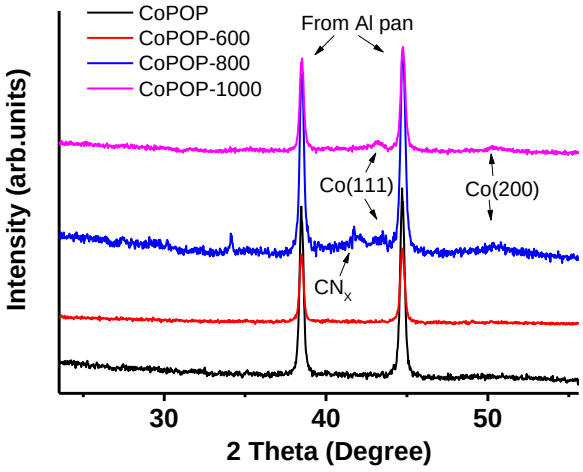

Fig. S6. Powder X-ray diffraction patterns of **CoPOP**, **CoPOP-600**, **CoPOP-800** and **CoPOP-1000**.

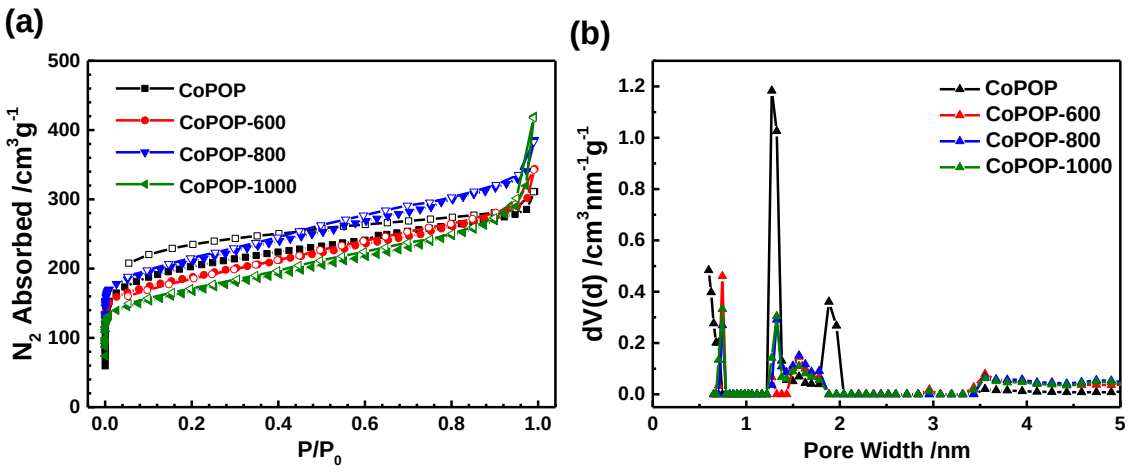

Figure S7. Nitrogen adsorption isotherms (77 K) (filled symbol: adsorption; hollow symbol: desorption) and corresponding pore size distribution of **CoPOP**, **CoPOP-600**, **CoPOP-800**, and **CoPOP-1000**.

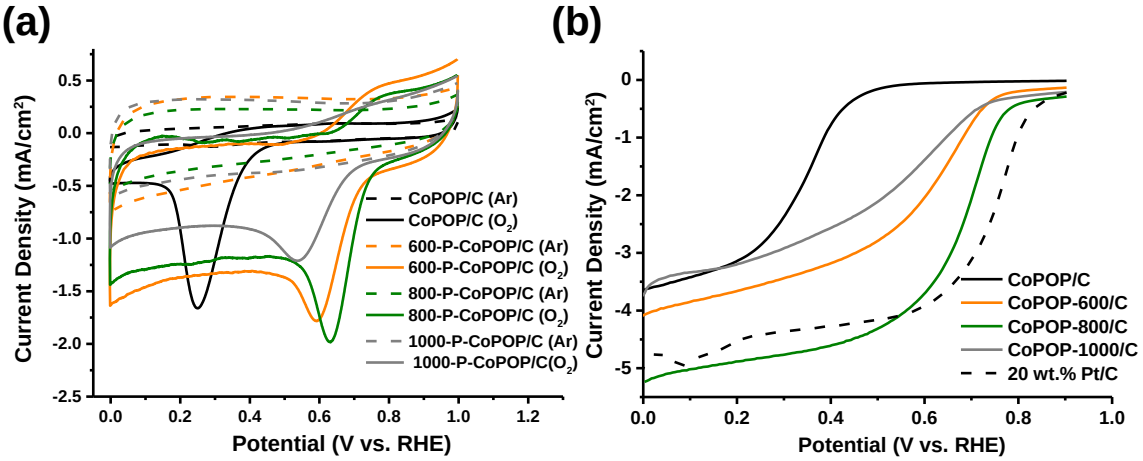

Figure S8. Cyclic voltammetry (CV) curves of **CoPOP/C**, **CoPOP-600/C**, **CoPOP-800/C**, and **CoPOP-1000/C** in 0.5 M H_2SO_4 (a); linear sweep voltammetry (LSV) curves of **CoPOP/C**, **CoPOP-600/C**, **CoPOP-800/C**, and **CoPOP-1000/C** and 20 wt% Pt/C in O_2-saturated 0.5 M H_2SO_4 (b). The scan rate was 10 mV s^{-1} for CV measurement, and 10 mV s^{-1} for RDE measurement.

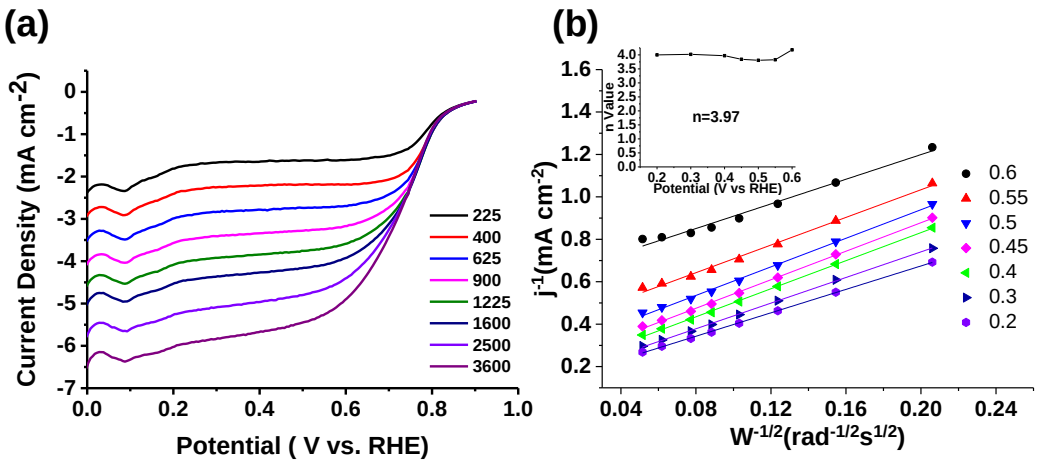

Fig. S9. LSV curves for 20 wt% Pt/C at different rotation rates in RDE measurements in O_2-saturated 0.5 M H_2SO_4 at 10 mV s^{-1}
and the corresponding Koutecky–Levich (K-L) plots (b). The insets in b show the average *n* values of 20 wt% Pt/C calculated from RDE against the electrode potential.

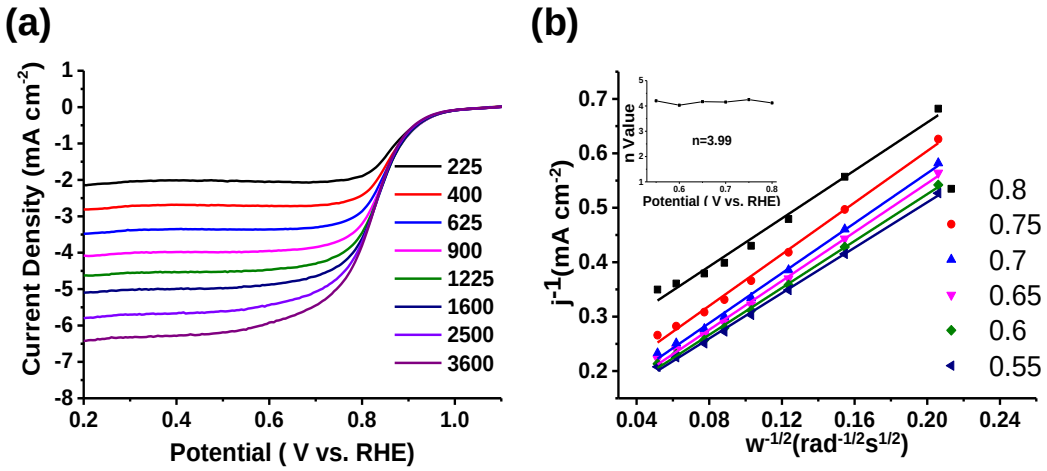

Fig. S10. LSV curves for 20 wt% Pt/C at different rotation rates in RDE measurements in O_2-saturated 0.1 M KOH at 10 mV s^{-1} and the corresponding Koutecky–Levich (K-L) plots (b). The insets in b show the average *n* values of 20 wt% Pt/C calculated from RDE against the electrode potential.

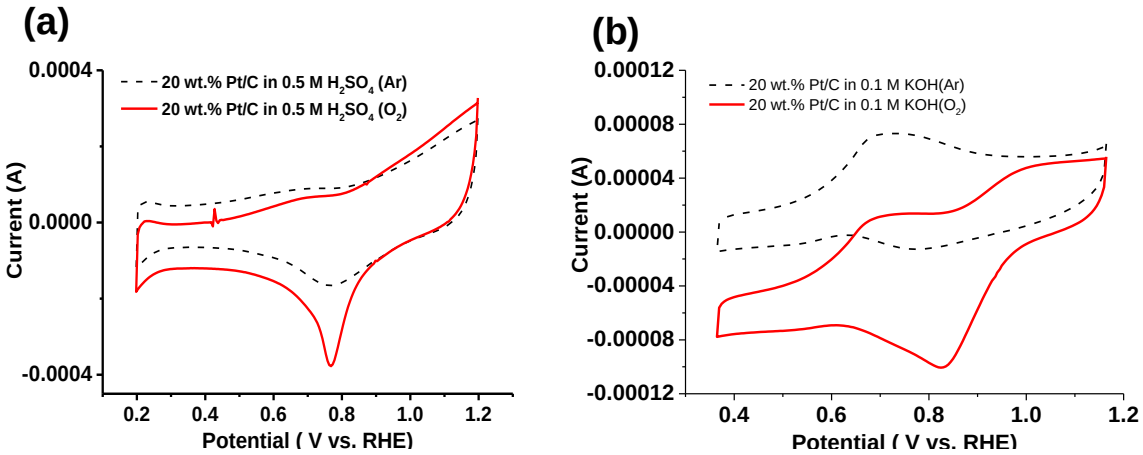

Fig. S11. CV curves of 20 wt% Pt/C in O_2- and Ar-saturated (a) 0.5 M H_2SO_4 and (b) 0.1 M KOH.

References

1 X. M. Liu, Y. H. Xu, Z. Q. Guo, A. Nagai and D. L. Jiang, *Chem. Commun.*, 2013, **49**, 3233-3235.

2 P. Pandey, O. K. Farha, A. M. Spokoyny, C. A. Mirkin, M. G. Kanatzidis, J. T. Hupp and S. T. Nguyen, *J. Mater. Chem.*, 2011, **21**, 1700-1703.