A Readily-Prepared, Convergent, Oxygen Reduction Electrocatalyst

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1. Preparation of polypyrrole/Co-TPP complex. (Co-TPP = Co-tetraphenylporphyrin)

The polypyrrole/Co-TPP was synthesized according to the procedures shown in Figure S1. A thin film of Iron (III) tosylate /Co-TPP was spin-coated onto ITO glass at a speed of 1000 rpm from a tetrahydrofuran solution containing 20% Iron (III) tosylate and 0.5 mM CoTPP. Then polyprrole was deposited onto Iron(III)/Co-TPP modified ITO glass *via* vapor phase polymerization.
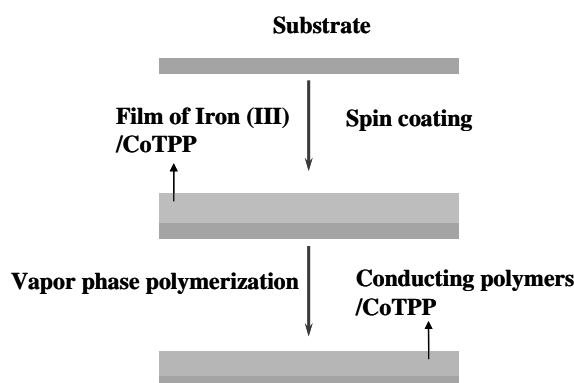

Figure S1. Schematic procedures for the preparation of PPy/Co-TPP.

2. Electrochemical measurements.

The electrochemical analysis was carried out as the following conditions. LSV was performed in a standard three-compartment cell (Figure S2) under an O_2 or N_2 atmosphere. The counter electrode was a platinum mesh separated from the working electrode by a glass-porosity frit. The reference electrode was an Ag/AgCl electrode. The electrolyte was a 0.5 M H_2SO_4 aqueous solution.
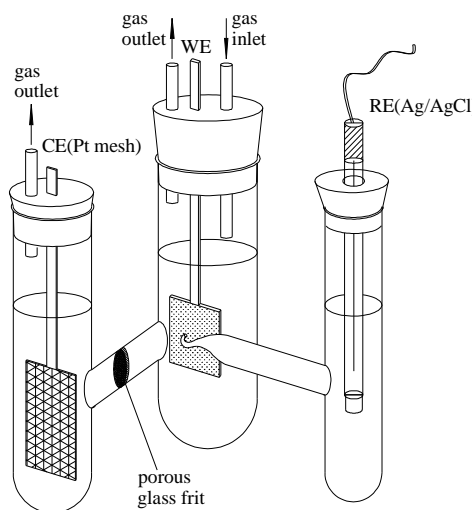
Figure S2. Cell schematic for electrochemical experiments.

3. Oxygen reduction at polypyrrole-CoTPP/ITO glass.

Figure S3 shows the LSVs of PPy/Co-TPP modified ITO glass recorded in N_2 and O_2 saturated 0.5 M H_2SO_4 solution. The catalysed oxygen reduction starts at 400 mV and the peak appears at approximately 300 mV (vs. Ag/AgCl). In comparison, no oxygen reduction was observed at N_2 saturated electrolyte.
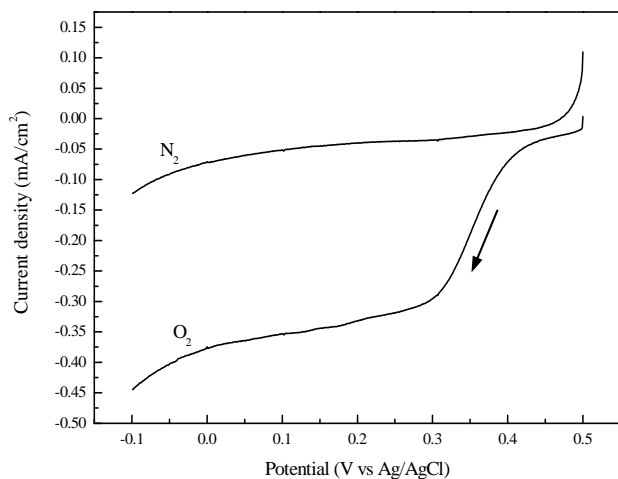
Figure S3. LSV for oxygen reduction at polypyrrole-CoTPP/ITO
glass in 0.5 M H_2SO_4. Scan rate 5 mV/s.
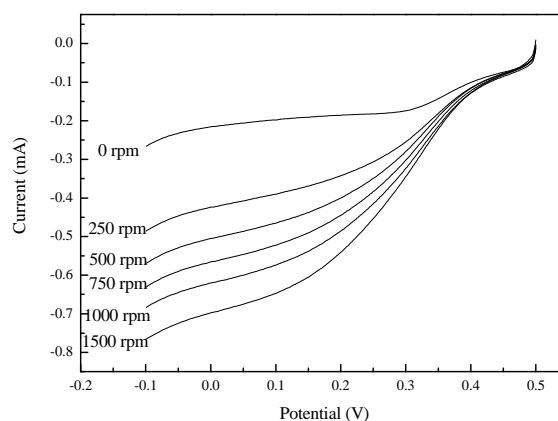
Figure S4. LSVs for oxygen reduction at PPy/Co-TPP in O_2 saturated 0.5 M H_2SO_4/H_2Oat different rotation speed. Scan rate 10 mV/s.

4.   RDE measurements.

Figure S4 shows the linear sweep voltammograms (LSVs) of oxygen reduction at PPy/Co-TPP modified glassy carbon electrode at different rotation speeds from 250 rpm to 1500 rpm. The Koutecky-Levich equation was used to determine the electrons number involved in oxygen reduction using PPy/Co-TPP. This equation is valid for a first-order process with respect to the diffusion species, and the current i is related to the rotation rate of the electrode ω according to

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{B\omega^{0.5}} \tag{1}$$

Where i_k is the kinetic current and B is Levich slope which is given by

$$B = 0.2nFA(D_{O_2})^{2/3}v^{-1/6}C_{O_2} \tag{2}$$

Here n is the number of electrons transferred in the reduction of one O_2 molecule, F is the Faraday constant ($F = 96485$ C/mol), A is the geometric area of electrode ($A = 0.24$ cm^2), D_{O_2} is the diffusion coefficient of O_2 ($D_{O_2} = 2.1 \times 10^{-5}$ cm^2 s^{-1}), v is the kinematics viscosity for sulfuric acid ($v = 1.07 \times 10^{-2}$ cm^2 s^{-1}) and C_{O_2} is concentration of O_2 in the solution ($C_{O_2} = 1.03 \times 10^{-3}$ mol dm^{-3}). The constant 0.2 is adopted when the rotation speed is expressed in rpm.

The kinetic current i_k can be obtained by extrapolation of the Koutecky-Levich plots (Figure S5) for $\omega^{-1/2} \to 0$. The electrons number and kinetic current calculated are given in Table 1. It can be seen from the table that the electrons exchanged deduced from these Koutecky-Levich plots is between 3.3 and 4.0 in the potential range from -50 mV to 100 mV.
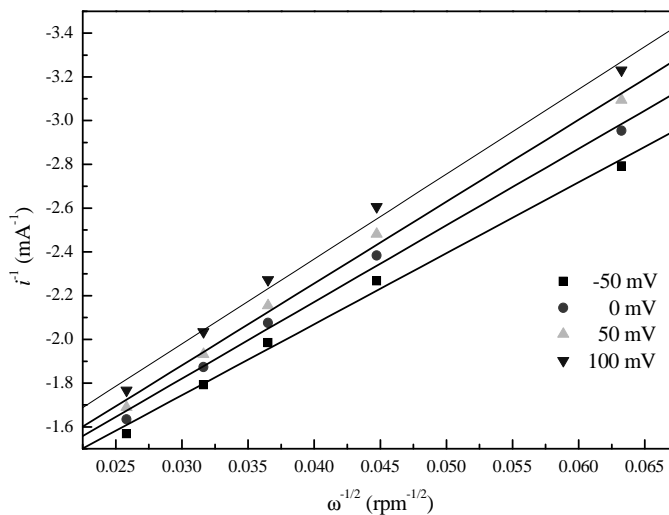
Figure S5. Koutecky-Levich plots for oxygen reduction at polypyrrole-CoTPP in 0.5 M H_2SO_4. Data taken from Figure S4.

Table 1

Slopes k_i of the Koutecky-Levich plots and corresponding number of electrons transferred obtained for the oxygen reduction at polypyrrole-CoTPP in O_2 saturated 0.5 M H_2SO_4 solution.

i	E_i/mV vs. Ag/AgCl	k_i	$1/i_k$ (mA^{-1})	n_i
1	-50	32.4	-0.771	4.0
2	0	35.0	-0.769	3.7
3	50	37.4	-0.759	3.5
4	100	38.8	-0.815	3.3

5.   RRDE measurements.

RRDE is a very effective method to make the product formed at disc electrode detectable at the ring electrode by convection from the disc to the ring electrode. It is also a powerful method to confirm how many electrons and what percentage of peroxide is involved in the oxygen reduction. The LSV curves were obtained under the same conditions as the RDE measurements except that the ring electrode was applied with a potential at 1.0 V. At this potential the hydrogen peroxide released during oxygen reduction at the disc electrode could be detected. Figure S6 depicts the LSV's for the ring and disk electrodes; at 200 mV, the ring current was 0.00837 mA, while the disk current was 0.275 mA. At 50 mV, the ring current was 0.01122 mA, while the disk current was 0.352 mA (graphical measures not depicted in Figure S6).
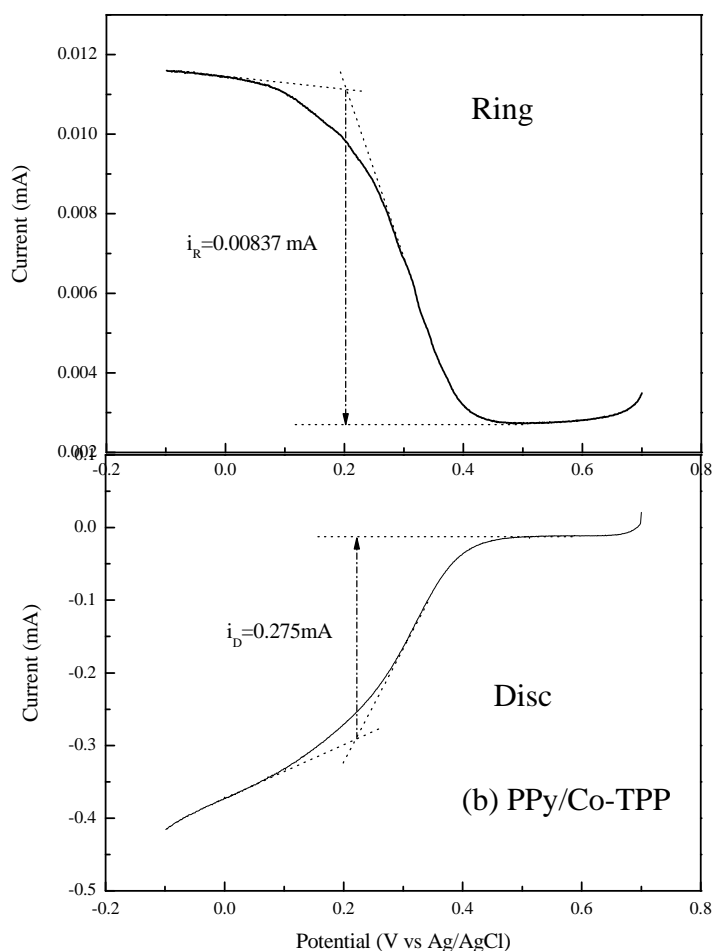
Figure S6. RRDE votammetry of oxygen reduction at a platinum electrode modified with PPy/Co-TPP in O_2 saturated 0.5 M H_2SO_4. Scan rate 10 mV/s.