Supplementary information

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1. Fig S1. Cyclic voltammograms of O_2 reduction at MWNTs/CoTMPyP/Pt hybrid film modified GC electrode with different scan rates: 0.02, 0.04, 0.06, 0.08, 0.10, 0.12, 0.14, 0.16, 0.18 and 0.20 V/s. Electrolyte: air-saturated 0.1M HAc-NaAc (pH 3.8) buffer solution. The inset shows the plot of the electrocatalytic oxygen reduction peak currents as a function of the square root of scan rates.

2. An EG&G PARC model 636 rotating ring disk electrode system and EG&G PARC model 366 bipotentiostat were used for rotating disk and rotating ring-disk voltammetry experiments. A rotating GC disk-platinum ring electrode was used as a working electrode. The collection efficiency (N) of the ring electrode obtained by reducing ferricyanide at disk electrode was 0.1512.

Figure S2. (A) Current-potential curves of O_2 reduction at a RDE modified with one layer of MWNTs/CoTMPyP/Pt hybrid film modified GC electrode with different rotating rate in air-saturated 0.1 M HAc-NaAc (pH 3.8) solution. (B) Koutecky-Levich plot of $i_1^{-1}-\omega^{-1/2}$ obtained from the RDE data of fig.S2(A). The dashed lines **a** and **b** were calculated for the diffusion-convection controlled reduction of O_2 by two (n=2) or four (n=4) electrons.

From the figure S2, the slope of the Koutecky-Levich plot is very close to that calculated for the four-electron reduction of O_2 to H_2O (dashed line in figure S2B(**b**), and the number of electron transfer for oxygen reduction at MWNTs/CoTmPyp/Pt hybrid film modified GC electrode was evaluated to be about 3.9, indicating mainly a 4e process of oxygen reduction.

Figure S3. Rotating ring-disk electrode voltammograms of one layer of MWNTs/CoTMPyP/Pt hybrid film modified GC electrode (scan rate 20mV s⁻¹, ω =100 rpm) in air-saturated 0.1 M HAc-NaAc (pH 3.8) solution. The potential of the platinum ring electrode was set to 1.0 V in order to oxidize H₂O₂ to O₂ completely.

From the figure S2,the number of electron transfer for oxygen reduction at one layer of MWNTs/CoTmPyp/Pt hybrid film modified GC electrode was evaluated to be about 3.6, which is consistent with the result from RDE experiment. This confirmed the conclusion that mainly a 4e process of oxygen reduction at one layer of MWNTs/CoTMPyP/Pt hybrid film modified GC electrode.

Supplementary information



Fig. S1



Fig. S2



Fig. S3