Supplementary information

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Title: Preparation of hybrid thin film modified carbon nanotubes on glassy carbon electrode and its electrocatalysis for oxygen reduction

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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\(_2\)O (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$^{-1}$, $\omega$ =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 $\text{H}_2\text{O}_2$ to $\text{O}_2$ 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