Electronic Supplementary Information

A novel cobalt tetranitrophthalocyanine/graphene nanocomposite assembled by an in situ solvothermal synthesis method as a highly efficient electrocatalyst for the oxygen reduction reaction in alkaline modium

medium

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1. Supplementary data



Fig. S 1 FT-IR spectra of PGr, CoTNPc, and CoTNPc/PGr.



Fig. S 2 (a) Cyclic voltammograms (CVs) of five different glassy carbon electrodes (Each electrode was loaded 12 μ g CoTNPc/PGr (4:1)) in 0.1 M NaOH solution saturated with O₂ at a scan rate of 50 mV s⁻¹. (b)-(f) Cyclic voltammograms of CoTNPc/PGr (4:1) in 5 mM Fe(CN)₆^{3-/4-}/1 M KCl at various scan rates from 20 to 240 mV s⁻¹. Inset: plot of peak current vs. (scan rate)^{1/2}.

The electrochemically assessible surface area can be estimated according to the Randles-Sevcik equation given below:¹

 $I_{pa} = 2.9\%$ $\ln AC_0 D^{1} v^2$

Where *D* and C_0 are the diffusion coefficient and bulk concentration of the redox probe (5 mM K₃[Fe(CN)₆]), respectively. *n* is the number of electron transferred (*n*=1),

 υ is the scan rate and *A* is the electrochemically assessible surface area. Cyclic voltammetry experiments at different scan rates were performed with CoTNPc/PGr modified GCE immersed in a solution of 5 mM K₃[Fe (CN)₆] containing 1 M KCl. These experiments are performed on five different glassy carbon electrodes. Each electrode is loaded 12 µg catalyst, respectively. The results are shown in Fig. S 2 (b)-(f). Consequently, the electrochemically assessible surface area of CoTNPc/PGr film on GCE was estimated according to the slope of the straight line of I_{pa} versus $\upsilon^{1/2}$, and the calculated results are given in Table S 1.

modified GCE. А $E_{\rm p, ORR}$ $I_{\rm p, ORR}$ $\dot{J}_{
m p, \, ORR}$ $[mA cm^{-2}]^a$ $[V]^a$ [mA]^a [cm²]^b 1 -0.225 0.124 0.095 -1.756 2 -0.225 0.124 0.090 -1.756 3 -0.226 0.121 0.102 -1.710 4 -0.226 0.125 0.101 -1.773 5 0.100 -0.231 0.126 -1.780 SE of mean^c 1.12×10⁻³ 1.87×10^{-3} 2.25×10^{-3} 1.22×10⁻² RSD^d 1.11 % 1.57 % 1.57 % 4.72 % a obtained from Supplementary Fig. S 2(a) b obtained from Supplementary Fig. S 2(b) c Standard error of mean d Relative standard deviation

Table S 1 The results of the quantitation of peak potential, peak current, electrochemically assessible surface area and peak current density of CoTNPc/PGr modified GCE.

Potential (V vs. SCE)		-0.200	-0.230	-0.250	-0.300	-0.350
	1	-1.497	-1.751	-1.656	-1.391	-1.233
Current Density (mA cm ⁻²)	2	-1.513	-1.755	-1.676	-1.424	-1.237
	3	-1.456	-1.707	-1.616	-1.332	-1.150
	4	-1.499	-1.773	-1.687	-1.416	-1.236
	5	-1.476	-1.779	-1.714	-1.443	-1.251
Mean		-1.488	-1.753	-1.670	-1.401	-1.221
SD		0.0222	0.0285	0.0366	0.0427	0.0406
SE of mean		9.99×10 ⁻³	1.27×10 ⁻²	1.64×10 ⁻²	1.92×10 ⁻²	1.81×10 ⁻²
Variance		4.93×10 ⁻⁴	8.09×10 ⁻⁴	1.34×10 ⁻³	1.82×10 ⁻³	1.65×10 ⁻³
RSD		1.49 %	1.62 %	2.19 %	3.05 %	3.32 %

Table S 2 The results of the current densities at different potentials.

Table S 3 The results of between-groups statistical differences of the current densities at different potentials by using SPSS analysis.

	ANOVA						
		16	VAR00001		<i>a</i> :		
	Sum of squares	df	Mean square	F	Sig.		
Between groups	0.901	4	0.225	183.723	1.83×10 ⁻¹⁵		
Within groups	0.025	20	0.001				
Total	0.925	24					

ANOVA								
	VAR00001							
	A subset of the set of $alpha = 0.05$)5		
	VAR00002	N	1	2	3	4	5	
Student-Newman-Keuls ^a	-0.23	5	-1.7530					
	-0.25	5		-1.6698				
	-0.20	5			-1.4882			
	-0.30	5				-1.4012		
	-0.35	5					-1.2214	
	Sig.		1.000	1.000	1.000	1.000	1.000	

Table S 4 The results of within-groups statistical differences of the current densities at different potentials by using SPSS analysis.

Will show the same subset of the set of the mean

a. Will use the harmonic mean sample size = 5.00

Current density (mA cm ⁻²)		-0.800	-1.000	-1.300	-1.500	-1.700
	1	-0.166	-0.177	-0.191	-0.200	-0.213
	2	-0.162	-0.175	-0.190	-0.200	-0.213
Potential	3	-0.166	-0.178	-0.192	-0.202	-0.222
$(\mathbf{V} \ \mathbf{VS}. \ \mathbf{SCE})$	4	-0.164	-0.178	-0.190	-0.200	-0.214
	5	-0.164	-0.176	-0.191	-0.201	-0.215
Mean		-0.164	-0.176	-0.191	-0.200	-0.216
SD		1.67×10 ⁻³	1.14×10 ⁻³	8.37×10 ⁻⁴	8.94×10 ⁻⁴	4.36×10 ⁻³
SE of mean		7.48×10 ⁻⁴	5.83×10 ⁻⁴	3.74×10 ⁻⁴	4.00×10 ⁻⁴	1.69×10 ⁻³
Variance		2.80×10 ⁻⁶	1.30×10 ⁻⁶	0.70×10 ⁻⁶	0.80×10 ⁻⁶	1.90×10 ⁻⁵
RSD		1.02 %	0.65 %	0.44 %	0.45 %	2.02 %

Table S 5 The results of the potentials at different current densities.

	ANOVA						
		I	/AR00003				
	Sum of squares	df	Mean square	F	Sig.		
Between groups	0.008	4	0.002	488.596	1.24×10 ⁻¹⁹		
Within groups	8.12×10 ⁻⁵	20	4.06×10 ⁻⁶				
Total	0.008	24					

Table S 6 The results of between-groups statistical differences of the potentials at different current densities by using SPSS analysis.

Table S 7 The results of within groups statistical differences of the potentials at different current densities by using SPSS analysis.

ANOVA								
VAR00003								
	VAD00004	N	А	subset of	the set of	alpha = 0.0	05	
	VAR00004	N	1	2	3	4	5	
Student-Newman-Keuls ^a	-1.70	5	-0.2154					
	-1.50	5		-0.2006				
	-1.30	5			-0.1908			
	-1.00	5				-0.1768		
	-0.80	5					-0.1644	
	Sig.		1.000	1.000	1.000	1.000	1.000	

Will show the same subset of the set of the mean

a. Will use the harmonic mean sample size = 5.00



Fig. S 3 (a) LSVs of the ORR on PGr in O₂-saturated 0.1 M NaOH with various rotation speeds at a scan rate of 10 mV s⁻¹. (b) K-L plots (according to Fig. S 3 (a)) at fixed potentials of -0.3, -0.4, -0.5, -0.6 and -0.7 V, respectively.



Fig. S 4 (a) LSVs of the ORR on CoTNPc in O_2 -saturated 0.1 M NaOH with various rotation speeds at a scan rate of 10 mV s⁻¹. (b) K-L plots (according to Fig. S 4 (a)) at fixed potentials of -0.3, -0.4, -0.5, -0.6 and -0.7 V, respectively.



Fig. S 5 (a) LSVs of the ORR on Pt/C in O_2 -saturated 0.1 M NaOH with various rotation speeds at a scan rate of 10 mV s⁻¹. (b) K-L plots (according to Fig. S 5 (a)) at fixed potentials of -0.3, -0.4, -0.5, -0.6 and -0.7 V, respectively.

	-0.7 V	-0.6 V	-0.5 V	-0.4 V	-0.3 V
1	2.82	2.48	2.23	2.07	1.87
2	2.95	2.57	2.30	2.14	2.14
3	2.80	2.46	2.23	2.11	2.03
4	2.90	2.55	2.28	2.14	2.12
5	2.54	2.27	2.09	2.00	1.90
SE of mean	7.09×10 ⁻²	5.32×10 ⁻²	3.67×10 ⁻²	2.63×10 ⁻²	5.53×10 ⁻²
RSD	5.6 %	4.8 %	3.6 %	2.8 %	6.1 %

Table S 8 The calculated electron transfer number at various potentials for PGr

	-0.7 V	-0.6 V	-0.5 V	-0.4 V	-0.3 V
1	3.03	2.78	2.73	2.72	2.69
2	2.69	2.60	2.52	2.30	2.80
3	3.12	2.65	2.65	2.72	2.82
4	2.63	2.54	2.49	2.52	2.60
5	2.72	2.61	2.52	2.45	2.46
SE of mean	9.89×10 ⁻²	4.01×10 ⁻²	4.62×10 ⁻²	8.09×10 ⁻²	6.66×10 ⁻²
RSD	7.7 %	3.4 %	3.6 %	7.1 %	5.6 %

Table S 9 The calculated electron transfer number at various potentials for CoTNPc

 Table S 10 The calculated electron transfer number at various potentials for

 CoTNPc/PGr

COINT C/T OF					
	-0.7V	-0.6V	-0.5V	-0.4V	-0.3V
1	3.96	3.86	3.81	3.73	3.60
2	4.08	3.98	3.83	3.71	3.74
3	4.02	3.89	3.76	3.66	3.66
4	4.00	3.98	3.83	3.71	3.74
5	3.93	3.81	3.76	3.67	3.62
SE of mean	2.58×10 ⁻²	3.36×10 ⁻²	1.59×10 ⁻²	1.33×10 ⁻²	2.94×10 ⁻²
RSD	1.4 %	1.9 %	0.9 %	1.8 %	0.8 %

References

1. M. Jahan, Q. Bao and K. P. Loh, J. Am. Chem. Soc., 2012, 134, 6707-6713.