Supplementary information



Fig. S1 Infrared spectra of SWNTs (black line), SWNTs-COOH (blue line) and 3 (red line).

It is noted that the SWNTs-COOH has the characteristic absorption peak of carboxyl and carbonyl between 1600 cm⁻¹ and 1700 cm⁻¹ and the broad absorption peak of hydroxy between 3300 cm⁻¹ and 3500 cm⁻¹ in the infrared spectra. This results demonstrate that these oxygen-containing functional groups have been covalently linked to SWNTs. Compared with the -COOH activated SWNTs, the infrared spectra of **3** showed strong stretching characteristic absorption peak of C-N and the horizontal vibration absorption of $-(CH_4)_n-(n\geq 4)$ at 720 cm⁻¹ in infrared spectra. This results



Fig. S2 Thermogravimetric curves of SWNTs, SWNTs-COOH, RB-0-CNT (1), RB-2-CNT (2) and RB-6-CNT (3).

There is not any reaction or change of mass when the stable SWNTs were heated under high temperature (red line). While, the mass of modified SWNTs were decreased under high temperature treatment, owning to the surface groups which was covalent linked with SWNTs are easily eliminated when it was treated by high temperature. All these results can provide some further evidences that RhB has been covalently linked to SWNTs.



Fig. S3 (a) Fluorescence intensity of 1 observed under different pH values; (b) Fluorescence intensity of 2 observed under different pH values; (c) Fluorescence intensity of 3 observed under different pH values.

As illustrated in Fig. S3, the fluorescence intensity of **1**, **2** and **3** was enhanced obviously when pH is lower than 3.60, indicated the ring-opening reaction happened for RhB covalently linked onto SWNTs. While, the ring-opening reaction of RhB alone occurred at pH = 4.0-5.0



Fig. S4 Dependence of the ECL intensity versus the concentration of NaOH with 1.0×10^{-6} mol/L RhB, 0.60 M KCl and 1.0×10^{-5} mol/L H₂O₂ at SWNT modified GC electrode, Scan rate = 100 mV/S.



Fig. S5 Dependence of the ECL intensity versus the concentration of KCl with 1.0×10^{-6} mol/L RhB, 1.0×10^{-5} mol/L H₂O₂ and 0.30 M NaOH at SWNT modified GC electrode, Scan rate = 100 mV/S.



Fig. S6 Dependence of the ECL intensity versus the logarithmic concentration of H_2O_2 with 1.0×10^{-6} mol/L RhB, 0.30 M NaOH and 0.60 M KCl at SWNT modified GC electrode, Scan rate = 100 mV/S.



Fig. S7 Dependence of the ECL intensity versus the logarithmic concentration of RhB with 1.0×10^{-6} mol/L H₂O₂, 0.30 M NaOH and 0.60 M KCl at SWNT modified GC electrode, Scan rate = 100 mV/S.



Fig. S8 Dependence of the ECL intensity versus the scan rate with 1.0×10^{-5} mol/L RhB, 1.0×10^{-6} mol/L H₂O₂, 0.30 M NaOH and 0.60 M KCl at SWNT modified GC electrode.



Fig. S9 Continuous cyclic scan of 3, the chemically modified GC electrode, for 10 cycles in aqueous solution containing 0.30 M NaOH, 0.60 M KCl and 1.0×10^{-6} mol/L H₂O₂ with 1.0×10^{-13} mol/L sodium sulfide.



Fig. S10 Dependence of the logarithmic Δ ECL increase versus the logarithmic concentration of sodium sulfide with 1.0×10^{-5} mol L⁻¹ RhB in aqueous solution containing 0.30 M NaOH, 0.60 M KCl and 1.0×10^{-6} mol L⁻¹ H₂O₂ at SWNT modified GC electrode



Fig. S11 Dependence of the logarithmic ECL increase versus the logarithmic concentration of sodium sulfide in aqueous solution containing 1.0×10^{-6} mol/L RhB, 0.30 M NaOH, 0.60 M KCl and 1.0×10^{-6} mol/L H₂O₂ at bare GC electrode.

No.	Concentration	Intraday precision	Interday precision
	(mol/L)	$Log(\Delta ECL)$	$Log(\Delta ECL)$
1	1.0×10 ⁻¹²	4.21	4.33
2	1.0×10 ⁻¹²	4.25	4.36
3	1.0×10 ⁻¹²	4.23	4.41
4	1.0×10 ⁻¹²	4.22	4.32
5	1.0×10 ⁻¹²	4.21	4.44
6	1.0×10 ⁻¹²	4.24	4.41
Mean		4.23	4.38
SD		0.02	0.02
RSD (%)		0.42	0.51

Table S1 The precision study results of 3, the chemically modified GC electrode detection method.^a

^{*a*} Average of three samples, each sample was measured repeatedly for at least 7 times, and the averaged readings were used.

No.	Concentration	Intraday precision	Interday precision
	(mol/L)	Log(ECL intensity)	Log(ECL intensity)
1	1.0×10 ⁻¹²	4.31	4.21
2	1.0×10 ⁻¹²	4.43	4.32
3	1.0×10 ⁻¹²	4.32	4.44
4	1.0×10 ⁻¹²	4.33	4.45
5	1.0×10 ⁻¹²	4.34	4.35
6	1.0×10 ⁻¹²	4.35	4.34
Mean		4.36	4.35
SD		0.10	0.13
RSD		2.3	3.1
(%)			

Table S2 The precision study results of SWNT modified GC electrode detection method^a

^{*a*} Average of three samples, each sample was measured repeatedly for at least 7 times, and the averaged readings were used.