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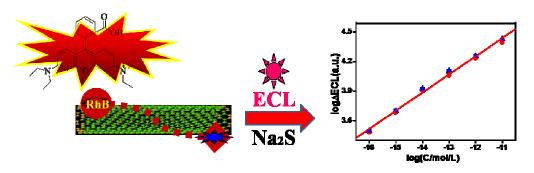
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Graphical Abstract



Rhodamine B (RhB) was covalently linked with SWNTs through different linkage and modified on glassy carbon (GC) electrode to detected sodium sulfide with good reproducibility and stability.

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ARTICLE TYPE

Determination of sodium sulfide based on electrochemiluminescence of Rhodamine B at a SWNT modified glassy carbon electrode

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Electrochemiluminescence (ECL) of Rhodamine B (RhB) at a single-wall carbon nanotube (SWNT) modified glassy carbon (GC) electrode has been employed for the determination of sodium sulfide. A linear response (R=0.99) over a sodium sulfide concentration range of 1.0×10⁻¹⁴~1.0×10⁻¹⁰ mol/L and detection limit of 1.0×10⁻¹⁴ mol/L can be reached. Furthermore, RhB was covalently linked with SWNT and then modified onto a GC electrode surface to detect sodium sulfide. It was found that the detection limit can be further reduced to 1.0×10⁻¹⁶ mol/L in the case of a RhB-hexamethylenediamine-SWNT modified GC electrode. This is much lower than other detection methods. The proposed method was applied to the determination of sodium sulfide added into deionized water; the recovery was quite satisfactory with good reproducibility and stability. All these results provide the possibility of developing a novel ECL detection method for sodium sulfide.

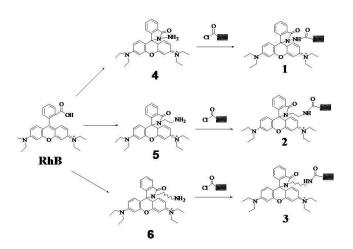
Introduction

Sulfide ions commonly exist in industrial waste, where they pollute the environment and damage human health due to the toxicity of hydrogen sulfide and the corresponding risks associated with exposure in a number of occupational settings. 1-3 Thus, determination of sulfide ions has achieved significant attention from the industrial, environmental, and biological point of view. In order to monitor the level of sulfide ions, many analytical methods such as titrimetric, 4,5 spectrophotometric, 6,7 amperometric, ⁸ polarographic, ⁹ ion chromatographic, ^{10,11} kinetics methods, 12-17 fluorescence method 18 and chemiluminescence 19-21 etc. have been developed. However, most of them are time-consuming and require some special training, so it has remained a challenge to develop a simple but reliable detection method for a rapid and sensitive determination of sulfide ions.

Rhodamine B (RhB, Scheme 1) is one of the xanthene dyes with intense fluorescence in solution. In recent years, the properties of RhB have been extensively studied²² and it is widely used in a variety of fields such as cell stain, 23-26 inorganic analysis, 27 active medium of dye lasers 28,29 bioanalytical chemistry30,31 etc, where RhB has been used as a chemiluminescent regents due to its unique photoluminescence property. In particular, RhB has been applied to detect VB1 (Vitamin B1)³², sodium sulfite³³ and sodium sulfide³⁴ based on its electrochemiluminescence (ECL) performance. For instance, Huang³⁴ and co-workers detected sodium sulfide based on ECL of RhB at a multi-wall carbon nanotube (MWNT) modified GC (glassy carbon) electrode. The ECL intensity varied linearly with sodium sulfide concentration from $6.0 \times 10^{-10} \sim 1.0 \times 10^{-8}$ mol/L. The detection limit (S/N=3) was 2.0×10⁻¹⁰ mol/L, and this is the lowest one till now.

Since its discovery by Lijima in 1991, 35 CNTs (carbon

nanotubes) have attracted more and more attention in chemical sensors and nanoscale electronic devices, owing to their ability to promote electron-transfer reactions. 36-38 Compared with MWNTs, SWNTs have better properties due to their larger superficial area. 39,40 In our previous works, 41 SWNT modified GC electrodes were used to study the ECL response of Ru(bpy)₃²⁺ for melamine, and the melamine detection limit was lowered to 1.0×10^{-13} mol/L. All these provide evidence that SWNTs are better electrode modification material.



Scheme 1 The structure of RhB and the synthetic routes of RhB chemically modified SWNTs

To continue research on this track and find a further application of SWNTs, sodium sulfide was detected using ECL of RhB at a SWNTs modified GC electrode. A linear response over a sodium sulfide concentration range of $1.0\times10^{-14}\sim1.0\times10^{-10}$ mol/L and detection limit of 1.0×10⁻¹⁴ mol/L was observed, which is 5 orders of magnitude lower than that of the aforementioned MWNT modified GC electrodes.34 To explore yet another application of the proposed method, RhB was covalently linked with SWNTs (Scheme 1) through a different linkage, and then modified onto a GC electrode surface to detect sodium sulfide. It was found that the detection limit can be further reduced to 1.0×10⁻¹⁶ mol/L in the case of a RhB-hexamethylenediamine-SWNT (3) modified GC electrode. This is 6 orders of magnitude lower than that of the aforementioned MWNT modified GC electrodes.

Experimental

Chemicals and reagents

Standard samples of RhB (99%), PVA (Polyvinyl alcohol, average M_w 17000, 99% hydrolyzed), HTAB (Hexadecyl trimethyl ammonium bromide) and thionyl choride were purchased from Sinopharm Chemical Reagent Co., Ltd. Shanghai, China. SWNTs samples were purchased from Shenzhen Nanotech Port Co. Ltd., China. Other chemicals and solvents were all of reagent grade and used as received.

The Acyl chlorination of SWNTs

The SWNTs were -COOH activated following the literatures procedure. 41,42 Typically, commercial SWNTs (250 mg) were refluxed in 500 ml of 2 M HNO3 for 2 days. Precipitation of SWNTs as solid was allowed to proceed overnight, and the clear solution above the suspension was then removed. The purified SWNTs were further oxidized by refluxing with 15 mL of 1:3 HNO₃/H₂SO₄ mixtures for 2 h at 120 °C. The suspension was washed 10 times with water after removel of the clear solution over the precipitates. Then the precipitates was filtrated and dried. The product was analyzed by infrared spectrometer, and the results are shown in Fig. S1

The acyl chloride of SWNTs were obtained by the reaction between -COOH activated SWNTs and thinoly chloride. 100 mg -COOH activated SWNTs was added into a two mouth flask, then 30 mL thionyl chloride was added. The mixture was dispersed with the aid of ultrasonic agitation 3 mL pyridine was added into the mixture as acid-binding agent. Then the mixture was heated and stirred under 70 °C for 24 h. After the reaction, the black powder was filtered and dried.

The Preparation of 1, 2 and 3

4. 5 and **6** were synthesized according to the literature method.⁴³ The RhB covalent functionalized SWNTs (1, 2 and 3) were obtained by the amidation reaction between 4/5/6 and acyl chloride of SWNTs^{39,40}. To demonstrate the interaction between RhB and SWNTs, 1, 2 and 3 were characterized by Infrared spectra (Here 3 was taken as an example), thermogravimetric analysis, and fluorescence detection. These results were presented in Fig.S1-Fig.S3.

Modified electrode preparation

GC working electrodes (3.0 mm in diameter) were first polished

with a slurry of 0.05 mm alumina, then sonicated, and rinsed with deionized water. Then the electrode was successively sonicated in 1:1 nitric acid and doubly distilled water, and allowed to dry at room temperature. An amount of 0.75 mg of the treated SWNTs/1/2/3 was dispersed with the aid of ultrasonic agitation in 5 mL DMF, then 1 mL of the solution was taken to mix with 2 mL of 5% PVA aqueous solution, to obtain a homogeneous, well-distributed suspension, then 10 μL of this suspension was dropped onto the surface of the pretreated GC electrode, and the solvent was allowed to evaporate at room temperature in the air.

Preparation of standard solution of sodium sulfide

The standard solution of sodium sulfide was prepared according to literature procedure. 4,21 The 0.10 mol/L standard stock solution of sodium sulfide was prepared by accurately weighting 0.088 g of sodium sulfide, added into a 10 mL volumetric flask and dissolved in 0.10 M NaOH solution. The stock solution was diluted with 0.10 M NaOH solution to obtain six standard solutions, 1.0×10^{-13} , 1.0×10^{-12} , 1.0×10^{-11} , 1.0×10^{-10} , 1.0×10^{-9} , 1.0×10⁻⁸ mol/L respectively. Because the sodium sulfide solution is instability, the standard solutions were prepared serially from the solution of next highest concentration and analyzed immediately.

ECL measurement

ECL measurements were performed on a MPI-B multifunctional ECL system from Xi'an Remex Analyse Instrument CO., Ltd., and the detecting method has been described elsewhere. 44-46 All experiments were carried out at room temperature. A commercial cylindroid quartz cell was used as an ECL cell, which contained a conventional three-electrode system consisting of modified electrode as the working electrode, a KCl-saturated Ag/AgCl electrode and a platinum wire electrode were used as the reference and the auxiliary electrode, respectively.

The corresponding standard solution (5.0 µL) of sodium sulfide was added into 5.0 mL of the aqueous solution containing 1.0×10⁻⁵ mol/L RhB, 0.30 M sodium hydroxide (NaOH), 0.60 M potassium chloride (KCl) and 1.0×10⁻⁶ M hydrogen peroxide (H₂O₂), and then the mixture was transferred to an ECL detection cell. The same procedure was followed in the case of 3, the chemically modified GC electrodes, except that 1.0×10⁻⁵ mol/L RhB was not added due to RhB has been covalently linked to SWNT. Cyclic potential sweep experiments were carried out in the potential region from 0 to 1.5 V and then back to 0, the ECL signals and CV vs. time were measured repeatedly for at least 5 times, and the average readings were used for the creation of plots.

Results and discussion

Effect of sodium hydroxide concentration on ECL

Sodium hydroxide (NaOH) can provide an alkaline environment for the ECL of RhB, and concentration of NaOH can affect the intensity of RhB ECL as reported. 47,48 The ECL performance of 1.0×10^{-6} mol/L RhB, 1.0×10^{-5} mol/L H₂O₂ and 0.60 M KCl under different concentrations of NaOH was investigated, the result is shown in Fig. S4. It is noted that the ECL intensity increased gradually along with the increasing concentration of NaOH. Both the highest ECL signal and the highest signal to background noise ratio were reached at 0.30 M NaOH. The measurements were repeated several times with a relative standard deviation (RSD) of less than 5.0%, suggesting good stability and reproducibility under these conditions. Hence the corresponding 0.30 M NaOH was chosen for the ECL measurement in the following experiments

Effect of potassium chloride concentration on ECL

The ECL performance of 1.0×10^{-6} mol/L RhB, 1.0×10^{-5} mol/L H_2O_2 and 0.30 M NaOH under different concentrations of KCl was investigated because the concentration of KCl is known to play an important role in RhB aqueous ECL reactions. ⁴⁹ The result is shown in Fig. S5. It is noted that the KCl concentration affected the ECL intensity of RhB dramatically at the SWNT modified GC electrode. Both the highest ECL signal and the highest signal to background noise ratio were reached at 0.60 M KCl. The measurements were repeated several times with a relative standard deviation (RSD) less than 5.0%, suggesting good stability and reproducibility under these condition, hence 0.60 M KCl was chosen for the ECL measurement in the following experiments.

Effect of hydrogen peroxide concentration on ECL

The ECL performance of 1.0×10^{-6} mol/L RhB, 0.30 M NaOH and 0.60 M KCl under different concentrations of H_2O_2 at a SWNT modified GC electrode was also investigated (Fig. S6). It was noted that the H_2O_2 concentration affected the RhB ECL over a wide range, which is in agreement with the literature. He highest ECL signal, best reproducibility and stability were shown for 1.0×10^{-6} mol/L H_2O_2 . Therefore, 1.0×10^{-6} mol/L H_2O_2 was employed for all the detections below.

Effect of RhB concentration on ECL

Considering RhB was used as luminescent reagent, its concentration could affect ECL measurement directly. The ECL performance at different concentrations of RhB was investigated in aqueous solution containing 0.30 M NaOH, 0.60 M KCl and $1.0\times10^{-6}\,\text{mol/L}\,\text{H}_2\text{O}_2$ and the result is shown in Fig. S7. It is noted that the highest ECL intensity can be achieved at $1.0\times10^{-5}\,\text{mol/L}$ RhB, while, the ECL intensity decreased along with the further increased concentration of RhB. Therefore, $1.0\times10^{-5}\,\text{mol}\cdot\text{L}^{-1}\,\text{RhB}$ was used for following ECL measurement.

Effect of scan rate on ECL

As indicated in the literature, 49,50 the scan rate could affect the ECL over a wide range, because the ECL efficiency significantly depends on the rate of generation/annihilation of the excited state * RhB. To investigate the effect of different scan rates on ECL intensity, ECL performance of 1.0×10^{-5} mol/L RhB, 1.0×10^{-6} mol/L H $_2$ O $_2$, 0.30 M NaOH and 0.60 M KCl under different scan rates was also investigated. The results are shown in Fig. S8. It is noted that the scan rate affected the ECL dramatically at the SWNT modified GC electrode, and that the best reproducibility and stability was reached when scan rate was 80 mV/s. Therefore, 80 mV/s was employed for all the detections below.

ECL performance

Cyclic voltammograms and the corresponding ECL performance of $1.0\times10^{-5}\,\text{mol/L}$ RhB in the solution containing $1.0\times10^{-6}\,\text{mol/L}$

H₂O₂, 0.30 M NaOH and 0.60 M KCl at a bare GC electrode (solid) and a SWNT modified GC electrode (dash) were investigated. The results are shown in Fig. 1. When the electrode potential was scanned positively close to 1.3 V, significant ECL signals were observed for the bare GC electrode and the SWNT modified GC electrode. Compared to the bare GC electrode, the SWNT modified GC electrode had a remarkable ECL enhancement, and this can be ascribed to the excellent electron transfer ability of SWNT.³⁶⁻³⁸

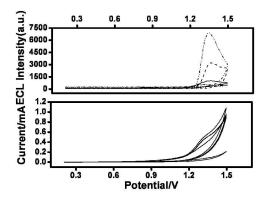


Fig. 1 ECL and cyclic voltammetric curves of 1.0×10^{-5} mol/L RhB in aqueous solution containing 1.0×10^{-6} mol/L H₂O₂, 0.30 M NaOH and 0.60 M KCl at bare GC electrode (solid); SWNT modified GC electrode (dash); **2** chemically modified GC electrode (dash dot); **3** chemically modified GC electrode (dash dot dot). Scan rate = 80 mV/s

To make a comparison, experiments on 2 (dash dot) chemically modified GC electrodes and 3 (dash dot dot) chemically modified GC electrodes (Fig.1) were also studied, and good reproducibility and stability was achieved when SWNT was 0.05 mg/mL and PVA was 3.40%.

As illustrated in Fig. 1, the cyclic voltammograms and the corresponding ECL performance of **2**, the chemically modified GC electrode, is similar to that of the bare GC electrode. Also, the cyclic voltammograms and the corresponding ECL performance of **3**, the chemically modified GC electrode exhibited the best results under the same conditions. In particular, its ECL intensity is 9.40 times higher than that of the bare GC electrode, indicating that the carbon chain linkage can affect the ECL performance of the chemically modified GC electrode to some extent. All these results can perhaps be explained by the carbon chain linkage can affect the electron transfer between SWNT and RhB to some extent, ⁵² the reason is still under investigation.

Linearity

In order to investigate the response of 3, the chemically modified GC electrode for sodium sulfide, the aqueous solution containing 1.0×10^{-6} mol/L H_2O_2 , 0.30 M NaOH and 0.60 M KCl was titrated with different concentrations sodium sulfide. As shown in Fig. 2, upon addition of sodium sulfide into the solution, the ECL intensity increased gradually.

A good linear calibration curve (Fig. 3) between the logarithm of ΔECL ($\Delta ECL=ECL_{after~addition~sodium~sulfide}\text{-}ECL_{before~addition~sodium~sulfide})$ intensity and the logarithm concentration of Na_2S (log[Na_2S]) can be established over the concentration range $1.0\times10^{-16}-1.0\times10^{-11}~\text{mol/L}$ for Na_2S .

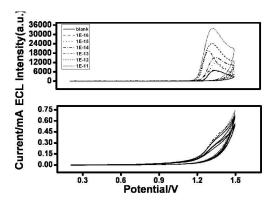


Fig. 2 ECL and cyclic voltammetric response of **3** chemically modified GC electrode for 0 (solid), 1.0×10^{-16} mol/L (dash), 1.0×10^{-15} mol/L (dot), 1.0×10^{-14} mol/L (dash dot), 1.0×10^{-12} mol/L (dash dot dot) and 1.0×10^{-11} mol/L (short dash) sodium sulfide in the aqueous solution containing 1.0×10^{-6} mol/L H_2O_2 , 0.30 M NaOH and 0.60 M KCl.

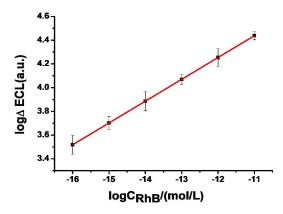


Fig. 3 Dependence of the logarithmic ΔECL increase versus the logarithmic concentration of sodium sulfide in the aqueous solution containing 0.30 mol/L NaOH, 0.60 mol/L KCl and 1.0×10^{-6} mol/L H₂O₂ at 3 chemically modified GC electrode. Scan rate=80 mV/s.

The regression equation was $log\Delta ECL = 6.46 + 0.18 log[Na_2S]$ (equation 1) with a linear coefficient R=0.99, the detection limit was down to 1.0×10^{-16} mol/L, this is 6 orders of magnitude lower than that of the reported lowest detection limit $(2.0\times10^{-10} \text{ mol/L})$, $^{4-21}$ suggesting that 3, the chemically modified GC electrode, can be suitable to detect Na₂S in aqueous solution.

Fig. S9 shows the ECL performance by immersing the 3, the chemically modified GC electrode, in aqueous solution containing 0.30 mol/L NaOH, 0.60 mol/L potassium chloride and 1.0×10^{-6} mol/L hydrogen peroxide with 1.0×10^{-13} mol/L sodium sulfide, then continuously cyclic potential scanning for ten times at the scan rate of 80 mV/s. No significant change of the ECL intensity was observed in the detection process, suggesting good reproducibility and stability of the ECL measurement on the 3, the chemically modified GC electrode.

Meanwhile, 1.0×10^{-5} mol/L RhB was titrated with different concentrations of sodium sulfide in the aqueous solution containing 0.30 mol/L NaOH, 0.60 mol/L KCl and 1.0×10^{-6} mol/L H₂O₂ at a SWNT modified GC electrode (Fig. S10). There also existed a good linearity between the logarithm of Δ ECL

 $(\Delta ECL=ECL_{after}\ addition\ sodium\ sulfide}-ECL_{before}\ addition\ sodium\ sulfide})$ intensity and the logarithm concentration of Na₂S (log[Na₂S]). The regression equation was log $\Delta ECL=5.34+0.18$ log[Na₂S] (equation 2) with a linear conefficient R=0.99. The detection limit was 1.0×10^{-14} mol/L for Na₂S, which is also lower than other detection methods. Although covalent linkage might affect the sp² structure of the SWNTs, and therefore their electronic properties, 2 order lower detection limit can be reached in comparison with noncovalent approaches.

For the bare GC electrode (Fig. S11), a linear calibration curve between the logarithm of ΔECL ($\Delta ECL=ECL_{after~addition~sodium~sulfide}$) intensity and the logarithm concentration of Na₂S (log[Na₂S]) can be established over the concentration range $1.0\times10^{-9}-1.0\times10^{-5}~mol/L$, and the detection limit is $1.0\times10^{-9}~mol/L$. At least 7 orders of magnitude difference existed compared with that of 3, the chemically modified GC electrode. All these demonstrated the advantage of 3, the chemically modified GC electrode.

Determination of the recoveries.

Table 1 The recoveries of sodium sulfide added into a deionized water samples were detected by **3**, the chemically modified GC electrode (No. 1, 2, 3) and the SWNT modified GC electrode (No. 4, 5, 6) in aqueous solution containing 0.30 mol/L NaOH, 0.60 mol/L KCl and 1.0×10^{-6} mol/L $\rm H_2O_2$.^a

No.	Added	Detected	Average	Recovery	RSD
	(mol/L)	(mol/L)	(mol/L)	(%)	(%)
1	5.0×10 ⁻¹⁶	4.95×10 ⁻¹⁶			
	5.0×10 ⁻¹⁶	4.95×10 ⁻¹⁶	4.97×10 ⁻¹⁶	99.40%	0.80%
	5.0×10 ⁻¹⁶	5.02×10 ⁻¹⁶			
2	1.0×10 ⁻¹³	1.00×10 ⁻¹³			
	1.0×10 ⁻¹³	1.10×10 ⁻¹³	1.07×10 ⁻¹³	107.00%	5.20%
	1.0×10 ⁻¹³	1.10×10 ⁻¹³			
3	1.0×10 ⁻¹¹	1.08×10 ⁻¹¹			
	1.0×10 ⁻¹¹	1.07×10 ⁻¹¹	1.10×10 ⁻¹¹	110.00%	1.40%
	1.0×10 ⁻¹¹	1.10×10 ⁻¹¹			
4	1.0×10 ⁻¹⁴	1.00×10 ⁻¹⁴			
	1.0×10 ⁻¹⁴	1.10×10 ⁻¹⁴	1.00×10 ⁻¹⁴	103.00%	5.80%
	1.0×10 ⁻¹⁴	1.00×10 ⁻¹⁴			
5	1.0×10 ⁻¹²	1.00×10 ⁻¹²			
	1.0×10 ⁻¹²	1.10×10 ⁻¹²	1.03×10 ⁻¹²	103.00%	6.10%
	1.0×10 ⁻¹²	0.99×10^{-12}			
	1.0×10 ⁻¹⁰	1.10×10^{-10}			
6	1.0×10 ⁻¹⁰	1.20×10 ⁻¹⁰	1.16×10 ⁻¹⁰	116.00%	5.80%
	1.0×10 ⁻¹⁰	1.20×10 ⁻¹⁰			

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

In order to assess the accuracy of the proposed method, it was applied to the determination of sodium sulfide added into deionized water. Three deionized water samples with different concentrations of sodium sulfide were studied for 3, the chemically modified GC electrode and the SWNT modified GC electrode. $5.0~\mu L$ of the sample was added into 5.0~mL of the the aqueous solution containing 1.0×10⁻⁵ mol/L RhB, 0.30 mol/L sodium hydroxide, 0.60 mol/L potassium chloride and 1.0×10⁻⁶ mol/L hydrogen peroxide. The same procedure was followed in the case of 3, the chemically modified GC electrodes, except that 1.0×10⁻⁵ mol/L RhB was not added due to RhB has been covalently linked to SWNT. The ECL intensity was checked and the concentration of sodium sulfide was calculated according to the established regression equations (The regression equation 1 for 3, the chemically modified GC electrodes, the regression equation 2 for SWNT modified GC electrodes). The analytical results are shown in Table 1.

It is noted that the recovery is quite satisfied for both 3, the chemically modified GC electrode (No. 1, 2, 3) and the SWNT modified GC electrode (No. 4, 5, 6). The relative deviations of less than 6.10% showed the fine accuracy.

It takes no more than 90 min to get a result for a deionized water sample (from sample preparation to get an analytical data) and the operator only need to follow a scheduled procedure after the method was built up (all the detecting condition and linearity and calibration curves have been settled down).

Interference study

To further assess the application ability of the proposed method for the analysis of sodium sulfide in real samples, the interference effects of coexistence substances, which were expected to be present in the samples, were also examined. The solution used for this purpose contain 0.30 mol/L sodium hydroxide, 0.60 mol/L potassium chloride, 1.0×10^{-6} mol/L hydrogen peroxide, 5.0×10^{-14} mol/L sodium sulfide and interfering ion. To eliminate interference from some metal ions under a basic environment, EDTA (Ethylene diamine tetraacetic acid). EGTA (Ethylene glycol tetraacetic acid) or citrate can be added into the detection system, if necessary.³⁴ A species was not considered to make much interference if it caused a relative error of no more than ±5.0% in the measurement of 5.0×10⁻¹⁴ mol/L sodium sulfide.³⁴ The tolerable concentration for detecting 5.0×10⁻¹⁴ mol/L sodium sulfide were determined as follows: 5.0×10⁻⁴ mol/L for K⁺, SO₄²⁻, SO₃²⁻, Cl⁻, PO₄³⁻, CO₃²⁻, C₂O₄²⁻, CH₃COO⁻, I⁻, NO₂⁻, F⁻, EDTA, EGTA; 5.0×10⁻⁵ mol/L for citrate, glucose; 4.0×10⁻¹⁰ mol/L for ascorbic acid.

Precision studies

In order to access the experimental precision, we employed 1.0×10⁻⁵ mol/L RhB and 3, the chemically modified GC electrodes to analyze the sample containing 1.0×10⁻¹² mol/L sodium sulfide according to the method mentioned in experimental section in the aqueous solution containing 0.30 M sodium hydroxide, 0.60 M potassium chloride and 1.0×10⁻⁶ M H₂O₂. The values of relative standard deviation for intra and inter-day variation are given in Table S1 (The precision studies results of 3, the chemically modified GC electrode detection method) and Table S2 (The precision studies results of SWNT modified GC electrode detection method).

It is noted that the precision was quite satisfied for SWNT modified GC electrode and 3, the chemically modified GC electrodes. The relative standard deviations less than 3.10 % for sodium hydroxide showed the fine precision.

Conclusions

In conclusion, ECL of RhB at a SWNT modified GC electrode has been successfully employed for the determination of sodium sulfide, the sodium sulfide detection limit is 1.0×10^{-14} mol/L. Meanwhile, RhB was covalently linked with SWNT and then modified onto GC electrode to detect sodium sulfide, the detection limit can be further down to 1.0×10⁻¹⁶ mol/L. The recovery was quite satisfactory with good reproducibility and stability. All these results provide the possibility of developing a novel ECL detection method for sodium sulfide.

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Notes and references

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- † Electronic Supplementary Information (ESI) available: [The supplementary information includes the results of Infrared spectra, thermogravimetric analysis, and fluorescence detection; The result of experimental conditions optimization]. See DOI: 10.1039/b000000x/
- 1 B. Predmore, D. Lefer, G. Gojon, Redox Signaling, 2012, 17, 119.
- 2 K. Eto, T. Asada, K. Arima, T. Markifuchi, H. Kimura, Biochem. Biophys. Res. Commun., 2002, 293, 1485.
- 3 S. Fiorucci, E. Antonelli, A. Mencarelli, S. Orlandi, B. Renga, G. Rizzo, E. Distrutti, V. Shah, A. Morelli, Hepatology, 2005, 42, 539.
- 4 L. Ebdon, S. J. Hill, M. Jameel, W. T. Corns, P. B. Stock-well, Analyst, 1997, 122, 1225.
- 5 M. Sarwar, M. Elahi, M. Anwar, M. Hanif, Mikrochim. Acta., 1970, 12, 846
- 6 C. F. Wood, I. L. Marr, Analyst, 1988, 113, 1635.
- 7 S. Knmatsu, A. J. Shundo, Chem. Soc. Rev., 1967, 84, 1679.
- 8 J. Kurzawa, Anal. Chim. Acta., 1985, 173, 343.
- 9 D. R. Canterfold, Anal. Chem., 1975, 47, 88.
- 10 K. Han, W. F. Koch, Anal. Chem., 1987, 59, 1016
- 11 R. J. Williams, Anal. Chem., 1983, 55, 851.
- 12 A. Safavi, M. Mirzaee, J. Fresenius, Anal. Chem., 2000, 367, 645.
- 13 A. Safavi, Z. Ramazzani, Talanta, 1997, 44, 1225.
- 14 H. Weisz, T. Lenz, Anal. Chim. Acta., 1974, 70, 359.
- 15 M. F. Mousavi, M Shamsipur, Bull. Chem. Soc. Jpn., 1992, 65, 2770.
- 16 M. F. Mousavi, N. Sarlack, Anal. Lett., 1997, 30, 1567.
- 17 A. A. Ensafi, M. Samimifar, Anal. Lett., 1994, 27, 153.
- 18 J. R. Femandez, J. M. Costa, R. Pereiro, A. S. Medel, Anal. Chim. Acta., 1999, 398, 23.
- 19 S. R. Spurlin, E. S. Yeung, Anal. Chem., 1982, 54, 320.
- 20 J. X. Du, Y. H. Li. J. R. Lv, Anal. Chim. Acta., 2001, 448, 79.
- 21 A. Safavi, M. S. Karimi, Talanta, 2002, 57, 491.
- 22 V. Dujols, F. Ford, A. W. Czarnik, J. Am. Chem. Soc., 1977, 119, 7386.
- 23 I. Rustenbeck, C. Dikel, C. Herrmann, T. Grimmsmann, Biosci. Rep., 199. 2. 89.
- 24 H. N. Kim, M. H. Lee, H. J. Kim, J. S. Kim, J. Yoon, Chem. Soc. Rev., 2008, 37, 1465.
- 25 J. F. Zhang, J. S. Kim, Anal. Sci., 2009, 25, 1271.
- 26 Y. K. Yang, K. J. Yook, J. Tae, J. Am. Chem. Soc., 2005, 127, 16760.
- 27 M. J. Culzoni, A. Munoz de la Pena, A. Machuca, H. C. Goicoechea, R.

- Babiano, Anal. Method, 2013, 5, 30.
- 28 D. A. Hinckly, P. G. Saybold, D. P. Borris, Spectrochim. Acta., 1986, 42A, 747.
- 29 K. Mandal, T. D. L. Pearson, J. N. Demas, Anal. Chem., 1980, 52, 2184.
- 30 Y. J. Ma, M. Zhou, X. Y. Jin, B. Z. Zhang, H. Chen, N. Y. Guo, Anal. Chim. Acta., 2002, 464, 289.
- 31 H. Chen, M. Zhou, X. Y. Jin, Y. M. Song, Z. Y. Zhang, J. Ma. Anal. Chim. Acta., 2002, 478, 31.
- 32 C. X. Zhou, G. J. Zhang, Z. J. Zhang, Anal. Chim. Acta., 1999, 394, 165.
- 33 M. N. Zhang, C. X. Zhang, H. L. Qi, Microchim. Acta, 2004, 144, 155.
- 34 R. F. Huang, X. W. Zheng, Y. J. Qu, Anal. Chim. Acta., 2007, 582, 267.
- 35 S. Lijima, Nature (London), 1991, 354, 56.
- 36 J. Wang, M. Li, Z. S, N. Li, Z. Gu, Electroanalysis, 2002, 14, 223.
- 37 J. Wang, M. Li, Z. S, N. Li, Z. Gu, Anal. Chem., 2002, 74, 993.
- 38 Z. Wang, J. Liu, Q. Liang, Y. Wang, G. Luo, Analyst, 2002, 127, 653.
- 39 H. R. Darabi, M. J. Tehrani, K. Aghapoor, F. Mohsenzadeh, R. Malekfar, Appl. Surf. Sci., 2012, 258, 8953.
- 40 R. Martin, F. J. Cespedes-Guirao, M. D. Miguel, F. Fernandez-Lazaro, H. Garcia, A. Sastra-Santos, Chem. Sci, 2012, 3, 470.
- 41 F. Y. Liu, X. Yang, S. G. Sun, Analyst, 2011, 136, 374.
- 42 K. A. Williams, P. T. M. Veenhuizen, B. G. Torre, R. Eritja, C. Dekker, Nature, 2002, 420, 761.
- 43 X. Zhang, S. Sumiya, Y. Shiraishi, T. Hirai, J. Photochem. Photobio., A, 2009, 205, 215.
- 44 S. G. Sun, Y. Yang, F. Y. Liu, J. L. Fan, X. J. Peng, J. Kehr, L. Sun. Dalton Trans., 2009, 37, 7969.
- 45 S. G. Sun, Y. Yang, F. Y. Liu, J. L. Fan, J. Kehr, L. Sun, X. J. Peng, Dalton Trans., 2010, 39, 8626,
- 46 S. G. Sun, Y. Yang, F. Y. Liu, Y. Pang, J. L. Fan, L. Sun, X. J. Peng, Anal. Chem., 2009, 81, 10227.
- 47 N. W. Barnett, R. D. Gerardi, D. L. Hampson, R. A. Russell, Anal Commun., 1996, 33, 255.
- 48 Q. Song, G. M. Greenway, T. McCreedy, Analyst, 2001, 126, 37.
- 49 E. M. Zammit, G. J. Barbante, B. Carlson, E. H. Doevern, N. W. Barnett, C. F. Hogan, M. M. Richter, P. S. Francis, Analyst, 2012, 137, 2766
- 50 M. M. Richter, Chem. Rev., 2004, 104, 3003.
- 51 L. H. Guo, F. F. Fu, G. N. Chen, Anal. Bioanal. Chem., 2010, 399, 3323.
- 52 J. Li, Y. H. Xu, H. Wei, T. Huo, E. K. Wang, Anal. Chem., 2007, 79, 5439.