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Highly portable fluorescent turn-on sensor for Sulfide Anions based on Silicon nanowires

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By covalently modifying 3-[2-(2-Aminoethylamino)ethylamino]propyl-trimethoxysilane (ligand) and 4-Amino-1,8-naphthalic anhydride (fluorophore) onto the surface of silicon nanowires (SiNWs) and subsequently complexing it with cooper ion (Cu2⁺), a SiNWs-based fluorescent sensor for sulfide anions (S²⁻) was realized. Based on such ligand/Cu²⁺ approach, the new type of sensor realizes rapid sensing of S²⁻, and exhibits high sensitivity and selectivity for S²⁻ in water. Moreover, the as-prepared SiNW arrays-based sensor was successfully used in real time and in-situ monitoring of S²⁻ in running water by directly inserting it into the water. The present SiNW arrays-based sensor can be developed a portable commercial device applied in environmental analysis after further optimizing the technique and finely quantifying the response of the sensor.

Introduction

As a traditional toxic pollutant for environment, sulfide anion (S²⁻) exists widely in industrial settings, such as conversion into sulfur and sulfuric acid, production of wood pulp, dyes and cosmetic manufacturing, where it is either used as a reactant or generated as a byproduct. S²⁻ is also produced in biosystems due to the microbial reduction of sulfate by anaerobic bacteria or formation from the sulfur-containing amino acids in meat proteins.¹ Both of above industrial processes and biological metabolism would release S²⁻ into the water.² It has been reported that exposure to low concentration of S²⁻ could cause dizziness, while high concentration contact of S²⁻ would lead to unconsciousness, irritation in mucous membranes, permanent brain damage or even asphyxiation.³, ⁴ Moreover, once protonated, the S²⁻ can be turned into HS⁻ or H₂S and more toxicity would be produced. Therefore, developing a method to rapidly and sensitively detect S²⁻ is of great significance for environmental and industrial requirement.

Several techniques, such as titration⁵, inductively coupled plasma atomic emission spectroscopy⁶, ⁷, electrochemical methods⁸, ion chromatography⁹, fluorimetry¹⁰-¹² et.al. have been employed to detect S²⁻. Among these reported methods, fluorescence-based assay shows great advantages over others due to its high sensitivity, rapid detection and simplicity of operation. In the past few years, the strong reducing capacity and nucleophilicity of S²⁻ were often utilized to develop fluorescent probes for highly selective detection of S²⁻. However, these S²⁻ probes based on such approach always need a relatively long response time.¹³-¹⁵ Recently, the affinity between anion and metal ion was used to detect anions and showed excellent kinetics. It is well known that S²⁻ can react with copper ion (Cu²⁺) to form a very stable CuS species, which owns a extremely low solubility product constant Ksp=3.63 × 10⁻²⁹.¹⁶ Employing the Cu²⁺ binding sites on the organic fluorophores or fluorescent semiconductor quantum dots, as well as the strong affinity between S²⁻ and Cu²⁺, several fluorescent S²⁻ probes have been fabricated and a rapid detection for S²⁻ was realized.¹⁷-²⁴ Nevertheless, these fluorescent probes have not yet been integrated into a portable device, which would cause some inconvenience in environmental analysis. Developing a highly portable device and directly inserting it into the determinand would enable one to monitor the environmental pollution more conveniently. In order to realize a portable sensor device, anchoring the probe to the surface of carrier would be a rational strategy.²⁵,²⁶

Recent studies show that one-dimensional (1D) nanostructures would be a good candidate for a carrier to fabricate various sensor devices with enhanced sensitivity and selectivity.²⁷-²⁹ Among 1D nanostructures, silicon nanowires (SiNWs) are particularly favorable due to their stability, nontoxicity, and easy assembly as an array for the device.³⁰-³² Considering the virtues of the SiNWs and excellent kinetics of the Cu²⁺·S²⁻ affinity-based probes in S²⁻ detection, we covalently immobilize the 3-[2-(2-Aminoethylamino)ethylamino]propyl-trimethoxysilane (ligand) and 4-Amino-1,8-naphthalic anhydride (fluorophore) onto the surface of SiNWs, and subsequently complex it with Cu²⁺, a SiNWs-based fluorescent turn-on sensor for S²⁻ was realized. This new type of sensor exhibits excellent sensitivity with a low
detection limit of 0.88 μM, and good S²⁻ binding selectivity over other anions. Moreover, the as-prepared SiNW arrays-based sensor was successfully used in real time and in-situ monitoring of S²⁻ in running water by directly immersing it into the water. The present SiNW arrays-based sensor can be developed a portable commercial device applied in environmental analysis after further optimizing the technique and finely quantifying the response of the sensor. Furthermore, the methods used to construct the current S²⁻ sensor can be extended to realize other highly portable chem-sensor devices for environmental application.

![Fig. 1 The TEM image of SiNWs by CVD method](Image)

**Modification of SiNWs**

The as-prepared SiNWs were immersed in a mixture containing 7.5 mL concentrated H₂SO₄ (98%) and 2.5 mL 30% H₂O₂ (V/V=3:1) at 90 °C for 1.5 h and then cooled down to room temperature. After repeatedly washed with doubly distilled water, the clean SiNWs were immersed in a mixture of 5 mL H₂O, 1 mL 30% H₂O₂ and 1 mL NH₄OH (V/V/V=5:1:1) at room temperature for 2 h to bring Si-OH bonds on the surface of the SiNWs. Then the OH-terminated SiNWs were repeatedly rinsed with doubly distilled water and dried under vacuum at 50 °C for the following chemical modification.

The modification procedure of the SiNWs was shown in Scheme 1. 20 mg of dried SiNWs were dispersed into 8 mL anhydrous toluene (distilled) under nitrogen in a two-neck round bottomed flask, then 0.78 mmol of 3-A was added by syringe. The suspension was heated to 90 °C and stirred for 36 h. After cooling down to room temperature, the product (defined as 3-A-SiNWs) was collected by a micro filter and repeatedly washed by ethanol.

The as-prepared 3-A-SiNWs were suspended in a round flask containing 6 mL absolutely anhydrous ethanol under nitrogen, then 0.1mmol (21.2 mg) of 4-A was added. The mixture was stirred for 18 h at 80 °C. The product (defined as 4-A-SiNWs) were collected by filtration and repeatedly washed with ethanol. Unreacted organic materials were removed completely by monitoring the fluorescence of the washing liquid.

**Preparation of SiNW arrays**

The high-quality SiNW arrays were fabricated by the chemical etching (CE) method. A clean n-type silicon wafer with [100]...
orientation was immersed into the solution of 4.6 M hydrofluoric acid (HF) and 5 mM silver nitrate for 15 min to deposit Ag particles on its surface, and the particles would act as catalyst in the following etching process. Then the wafer attached with Ag particles was soaked into the etching solution consisting of 4.6 M HF and 0.2 M H₂O₂ at 50 °C for 20 min. After etching, the samples were immersed into a solution of condensed hydrochloric acid (HCl) and condensed nitric acid (HNO₃) (V:V=3:1) for 1 h to remove the Ag particles. Finally, the SiNW arrays were obtained after copiously rinsing with water and ethanol. The SEM images were shown in Fig. 2. The diameters of the SiNWs are in the range of 150-300nm, while the wire length is around 15μm.

Fig. 2 SEM images of the side view (left) and the top view (right) of the SiNW arrays by CE method.

Modification of SiNW arrays

The modifying procedures of SiNW arrays were the same as that of SiNWs obtained by CVD method. The modified SiNW arrays were defined as 4-A-SiNW arrays.

Results and discussion

Characterization of the modification procedure

The X-ray photoelectron spectroscopy (XPS) was used to characterize the modifications of the SiNWs. As shown in Fig. 3a, it was found that little nitrogen can be detected from the bare SiNWs, while abundant nitrogen can be observed from 3-A-SiNWs. These results reveal that the molecules of 3-A have been covalently modified onto the surface of the SiNWs. After the 3-A-SiNWs further reacted with 4-A, the surface nitrogen content and carbon content of the 4-A-SiNWs changed compared with 3-A-SiNWs. From the insets of Fig. 3, it can be determined that the contents of N, C and Si were 16.25%, 55.45% and 9.82% on the surface of 3-A-SiNWs, while 11.23%, 65.38% and 5.46% on the surface of 4-A-SiNWs. Because the content of Si changed slightly, it can be employed as a standard to evaluate N content (16.25%/9.82% < 11.23%/5.46%) and C content (55.45%/9.82% < 65.38%/5.46%). Thus the contents of N and C on the surface of 4-A-SiNWs were more than that on the 3-A-SiNWs. Furthermore, the N(1s) spectrum of 3-A-SiNWs depicted in Fig. 3a shows a peak at around 398.8eV corresponding to the C-N-H bonds from the 3-A. While the N(1s) spectrum of 4-A-SiNWs depicted in Fig. 3b can be deconvoluted into three peaks: a same peak at 398.8eV related to C-N-H bonds of the 3-A, a peak at 399.6eV related to C-N-H bonds of the amino group from the fluorophore, and a peak at 400.6eV related to the N-C bonds of naphthalic anhydride structure. These results potently verify that the 4-A molecules has been covalently modified onto the surface of the 3-A-SiNWs successfully.

Thermogravimetric analysis (TGA) was employed to determine the content of the organic molecules on the surface of modified SiNWs. From the mass loss of the samples (Table. S1), the amount of the organic molecules on the surface of modified SiNWs was estimated to be 8.5x10⁻⁴mol/g. The calculation method was following the literature.

Fluorescence response of 4-A-SiNWs to Cu²⁺

In order to investigate the binding between 4-A-SiNWs and Cu²⁺, the 4-A-SiNWs were dispersed into the HEPES-buffer to form a 50μg/mL suspended solution. After the Cu²⁺ with various concentrations were added into above 4-A-SiNWs suspended solution for 0.5 min, the fluorescent spectra were recorded as shown in Fig. 4a. The dependence of the fluorescence intensity of 4-A-SiNWs on Cu²⁺ concentration was inserted into Fig. 4a. It can be observed that the fluorescence intensity of 4-A-SiNWs gradually decreased with the increase of the Cu²⁺ concentration and finally reached at a plateau at around 14 μM. It reveals that the ligand-containing 4-A-SiNWs has bound with Cu²⁺ to form a 4-A-SiNWs/Cu²⁺ complex. The apparent binding constant K between the 4-A-SiNWs and Cu²⁺ was calculated to be 2.25x10⁵ by using a Langmuir-type
analysis and fluorescence titration data. The fluorescence response of 4-A-SiNWs to other metals ions such as Cu\textsuperscript{2+}, Cd\textsuperscript{2+}, Mg\textsuperscript{2+}, Al\textsuperscript{3+}, Co\textsuperscript{2+}, Na\textsuperscript{+}, Hg\textsuperscript{2+}, Mn\textsuperscript{2+}, K\textsuperscript{+}, Ni\textsuperscript{2+}, Pb\textsuperscript{2+}, Zn\textsuperscript{2+} were also measured and the results were shown in Fig. S1. From Fig. S1, it can be found that Cu\textsuperscript{2+} exhibited the most excellent fluorescence quenching character.

![Fluorescence response of 4-A-SiNWs (50µg/mL) in the presence of different concentrations of Cu\textsuperscript{2+} (0-14µM) and S\textsuperscript{2-} (30µM) in HEPES buffer (pH=7.0, 20mM). The insets in (a) and (b) show the fluorescence change at 545nm as a function of [Cu\textsuperscript{2+}] and [S\textsuperscript{2-}], respectively, \( \lambda_e = 430\text{nm} \). (c) The linear relationship between the fluorescence intensity and the S\textsuperscript{2-} concentration in the range of 0-25µM.](image)

**Fluorescence response of the 4-A-SiNWs/Cu\textsuperscript{2+} complex to S\textsuperscript{2-}**

To check the response of the 4-A-SiNWs/Cu\textsuperscript{2+} complex to S\textsuperscript{2-}, the 4-A-SiNWs was preincubated with Cu\textsuperscript{2+}, and then the fluorescence response of the 4-A-SiNWs/Cu\textsuperscript{2+} complex to S\textsuperscript{2-} was investigated after adding S\textsuperscript{2-} instantly. As shown in Fig. 4b, the fluorescence of the 4-A-SiNWs/Cu\textsuperscript{2+} complex system was enhanced gradually with the increase of the S\textsuperscript{2-} concentration, indicating the 4-A-SiNWs/Cu\textsuperscript{2+} complex could be a promising fluorescent turn-on sensor for S\textsuperscript{2-}. The dependence of the emission intensity at 545nm on the S\textsuperscript{2-} concentration was shown as inset of Fig. 4b. Furthermore, a good linear relationship in the range of 0-25µM was obtained (Fig. 4c), and the detection limit of the 4-A-SiNWs/Cu\textsuperscript{2+} complex for the determination of S\textsuperscript{2-} was calculated to 0.88µM.

Scheme 2 illustrates the proposed response mechanism of the S\textsuperscript{2-} sensor. The paramagnetic Cu\textsuperscript{2+} can bind with the ligand-containing 4-A-SiNWs to form a 4-A-SiNWs/Cu\textsuperscript{2+} complex, which would lead to the fluorescence quenching of the system. The S\textsuperscript{2-} added into the 4-A-SiNWs/Cu\textsuperscript{2+} complex system could coordinate with the Cu\textsuperscript{2+} to form the stable species CuS ((K\textsubscript{a}=3.63 \times 10^{-10}), which resulted in the revival of the fluorescence.

![Scheme 2 Proposed response mechanism of the S\textsuperscript{2-} sensor.](image)

To investigate the selectivity, the fluorescence response of the 4-A-SiNWs/Cu\textsuperscript{2+} complex toward the common anions in environment was investigated. As shown in Fig. 5a, addition of 1mM F\textsuperscript{-}, Br\textsuperscript{-}, Cl\textsuperscript{-}, I\textsuperscript{-}, NO\textsubscript{3}\textsuperscript{-}, HSO\textsubscript{4}\textsuperscript{-}, CO\textsubscript{3}\textsuperscript{2-}, CH\textsubscript{3}COO\textsuperscript{-}, PO\textsubscript{4}\textsuperscript{3-}, SO\textsubscript{4}\textsuperscript{2-}, NO\textsubscript{2}\textsuperscript{-}, SCN\textsuperscript{-}, S\textsubscript{2}\textsubscript{O}\textsubscript{3}\textsuperscript{2-}, SO\textsubscript{2}\textsubscript{3-} had little effect on the fluorescence emission from the sensing system. In contrast, addition of 30µM S\textsuperscript{2-} to the 4-A-SiNWs/Cu\textsuperscript{2+} system resulted in the obvious fluorescence enhancement. Furthermore, the fluorescence response of the 4-A-SiNWs/Cu\textsuperscript{2+} complex towards S\textsuperscript{2-} in the presence of these anions were also investigated (Fig. 5a). It can be observed that these competing anions have ignorable influences on the detection of S\textsuperscript{2-}. The results demonstrate that the 4-A-SiNWs/Cu\textsuperscript{2+} complex have sufficient selectivity for S\textsuperscript{2-} even coexisting with these competing anions. In addition, the pH effect on the sensor’s performance was also studied. As shown in Fig. 5b, the fluorescence responses of the complex towards S\textsuperscript{2-} were relatively stable in the pH range from 6 to 10. This result indicates that the current sensor can be used for S\textsuperscript{2-} monitoring in a wide pH range.
Fluorescence response of the highly portable SiNW arrays-based sensor device to S²⁻

To further evaluate the applicability of the SiNWs-based S²⁻ sensor in real sample, the fluorescent sensor was applied to determine the S²⁻ in running water. After the running water containing different concentrations of S²⁻ was added into the system, the fluorescence of the 4-A-SiNWs/Cu²⁺ complex was recorded instantly. From Table 1, it can be found that the recovery values are in the range of 95-103%, which indicates that the S²⁻ concentrations detected by the sensor are in good agreement with those added in the samples. The results also reveal that the composition of the running water does not have an obvious effect on the detection of S²⁻. According to World Health Organization, the maximum recommended S²⁻ concentration in drinking water is less than 500µg/L (about 15µM). With the detection limit of 0.88µM and the good linear range of 0-25µM, the sensor shows the potential in water quality monitoring.

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Table 1 Determination of sulfide anion in running water.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Amount of sulfide anion</th>
<th>Recovery(%)</th>
<th>RSD(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Added (M)</td>
<td>Found (M)</td>
<td></td>
</tr>
<tr>
<td>Running Water</td>
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<td>0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>5.11</td>
<td>102.2</td>
</tr>
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<td>9.69</td>
<td>96.9</td>
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<td>14.35</td>
<td>95.7</td>
</tr>
<tr>
<td></td>
<td>20.0</td>
<td>19.52</td>
<td>97.6</td>
</tr>
</tbody>
</table>

In order to explore the application of our SiNW arrays-based sensor for real-time and in-situ monitoring of S²⁻ in the determinand, the modified 4-A-SiNWs array was pre-incubated with Cu²⁺, then the unreacted Cu²⁺ was washed with deionized water and the SiNW arrays-based sensor device for S²⁻ was obtained. The sensor device was immersed into 1mL running water, then different concentrations of S²⁻ were added into the system. The fluorescent images of the sensor device before and after being treated with 50µM and 100µM S²⁻ were recorded by a fluorescence microscopy and the results were shown in Fig. 6. As expected, the addition of different concentrations of S²⁻ resulted in the obvious enhancement with different levels determined from the fluorescence observation of the sensor device. This phenomenon exhibits the potential application of the portable sensor device in real-time and in situ monitoring of S²⁻ in environmental analysis after finely quantifying the response of the device. It is well known that S²⁻ is not stable in water and can be easily transformed into other substances like a more toxic gas H₂S, which is always produced in some specific working environment. Therefore, the response of the sensor device to H₂S was also investigated. From Fig. S2, it was found that the fluorescence of the sensor device increased obviously after being treated with H₂S. This phenomenon implied the potential use of sensor device in monitoring of H₂S in the environment.

Conclusions

In summary, we have designed and configured a rational fluorescent turn-on sensor for S²⁻ based on SiNWs and SiNW arrays. The present sensor displayed a good linear relationship between the fluorescence intensity and S²⁻ concentration from 0 to 25µM, and exhibited high selectivity for S²⁻ against other common anions. In addition, the present S²⁻ sensor works well in a wide pH range. In view of all these merits, the SiNW arrays-based portable sensor device was successfully used in real time and in-situ monitoring of S²⁻ at micromolar concentration in 100% aqueous solution. This work paves a way to fabricate the portable sensor device for S²⁻ and exhibits potential application in environmental analysis.

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Notes and references

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