RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Journal Name

RSCPublishing

ARTICLE

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

Cite this: DOI: 10.1039/x0xx00000x

Huimin Wang,[a,b] Lixuan Mu,[a] Liangliang Jin,[a,b] Guangwei She,[a] Haitao Xu[a] and Wensheng Shi *[a]

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

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 (Cu^{2+}), a SiNWs-based fluorescent sensor for sulfide anions (S^{2-}) was realized. Based on such ligand/Cu^{2+} approach, the new type of sensor realizes rapid sensing of S^{2-}, and exhibits high sensitivity and selectivity for S^{2-} in water. Moreover, the as-prepared SiNW arrays-based sensor was successfully used in real time and in-situ monitoring of S^{2-} 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 (S^{2-}) 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. S^{2-} 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 S^{2-} into the water.[2] It has been reported that exposure to low concentration of S^{2-} could cause dizziness, while high concentration contact of S^{2-} would lead to unconsciousness, irritation in mucous membranes, permanent brain damage or even asphyxiation.[3, 4] Moreover, once protonated, the S^{2-} can be turned into HS^- or H_2S and more toxicity would be produced. Therefore, developing a method to rapidly and sensitively detect S^{2-} is of great significance for environmental and industrial requirement.

Several techniques, such as titration[5], inductively coupled plasma atomic emission spectroscopy[6, 7], electrochemical methods[8], ion chromatography[9], fluorimetry[10-12] et.al. have been employed to detect S^{2-}. 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 S^{2-} were often utilized to develop fluorescent probes for highly selective detection of S^{2-}. However, these S^{2-} 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 S^{2-} can react with copper ion (Cu^{2+}) to form a very stable CuS species, which owns a extremely low solubility product constant $K_{sp}=3.63 \times 10^{-36}$.[16] Employing the Cu^{2+} binding sites on the organic fluorophores or fluorescent semiconductor quantum dots, as well as the strong affinity between S^{2-} and Cu^{2+}, several fluorescent S^{2-} probes have been fabricated and a rapid detection for S^{2-} 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 Cu^{2+}-S^{2-} affinity-based probes in S^{2-} 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 Cu^{2+}, a SiNWs-based fluorescent turn-on sensor for S^{2-} was realized. This new type of sensor exhibits excellent sensitivity with a low detection limit of 0.88μM, and good S^{2-} binding selectivity over other anions. Moreover, the as-prepared SiNW arrays-based sensor was successfully used in real time and in-situ monitoring of S^{2-} 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 S^{2-} sensor can be extended to realize other highly portable chem-sensor devices for environmental application.

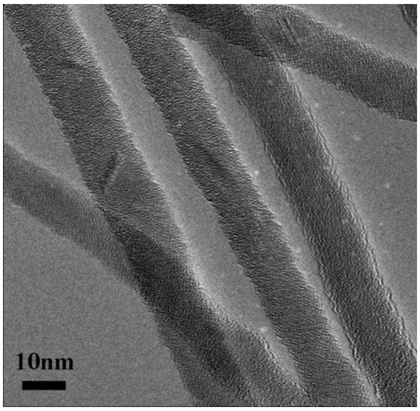


Fig. 1 The TEM image of SiNWs by CVD method

Experimental

Reagents and materials

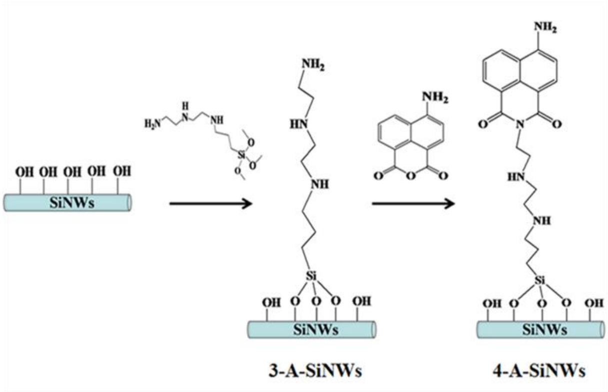
3-[2-(2-Aminoethylamino)ethylamino]propyl-trimethoxysilane (3-A) and 4-Amino-1,8-naphthalic anhydride (4-A) were purchased from Alfa Aesar. Other reagents were purchased from Beijing Chemical Regent Co. All reagents and chemicals were AR grade and used without further purifications. Water used for measurement was purified by Millipore filtration system. Sodium sulfide was used as the source of sulfide.

Measurements

Transmission electron microscopy (TEM) image was recorded by a JEOL-2100 at an acceleration voltage of 200KV. Scanning electron microscope (SEM) images were recorded by a Hitachi S-4800FEG. The X-ray photoelectron spectroscopy (XPS) was recorded by a PHIQUANTERA-II SXM at a voltage of 15KV. Fluorescence spectra were recorded on a Hitachi F-4600 spectrophotometer. Fluorescence images were taken with Olympus BX51TRF microscope (λ_{ex} =450nm-480nm).

Preparation of SiNWs

SiNWs were prepared by a typical chemical vapor deposition method (CVD) using silicon monoxide powder as the single source.[33] An alumina boat containing SiO powder (Aldrich，99%) was placed at the centre of a horizontal alumina tube mounted inside a high temperature tube furnace. The system was evacuated to 10^{-3} Pa. Mixture of Ar (95%) and H_2 (5%) as carrier gas was introduced at the flow rate of 49 sccm，then the system pressure was maintained at 800 Pa for ten minutes. And then the furnace was heated to 1350 °C，while the system pressure was maintained at 10^4 Pa. The system was maintained for 6 h and then cooled to room temperature naturally. The slightly yellow cotton-like product was collected at both sides of the alumina boat. The structures and morphologies of the as-prepared SiNWs were characterized using TEM. The SiNWs have a crystalline Si core of 10-12 nm in diameter and a silicon oxide sheath of 1-2 nm in thickness, as shown in Fig. 1.



Scheme 1 The procedure of SiNWs modification and the structure of 4-A-SiNWs.

Modification of SiNWs

The as-prepared SiNWs were immersed in a mixture containing 7.5 mL concentrated H_2SO_4 (98%) and 2.5 mL 30% H_2O_2 (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 H_2O, 1 mL 30% H_2O_2 and 1 mL NH_4OH (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.[34] 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 H_2O_2 at 50 ℃ for 20 min. After etching, the samples were immersed into a solution of condensed hydrochloric acid (HCl) and condensed nitric acid (HNO_3) (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.

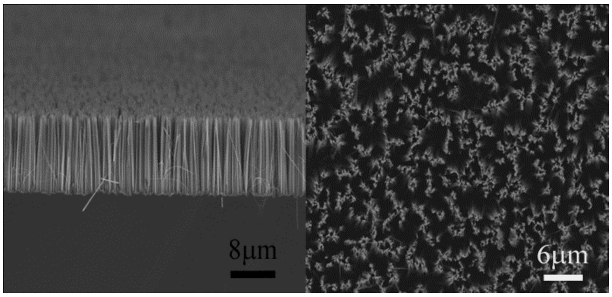


Fig. 2 SEM images of the side view (left) and the top view (right) of the SiNW arrays by CE method.

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.[35] 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.[36] 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 8.5×10^{-4}mol/g. The calculation method was following the literature.[37]

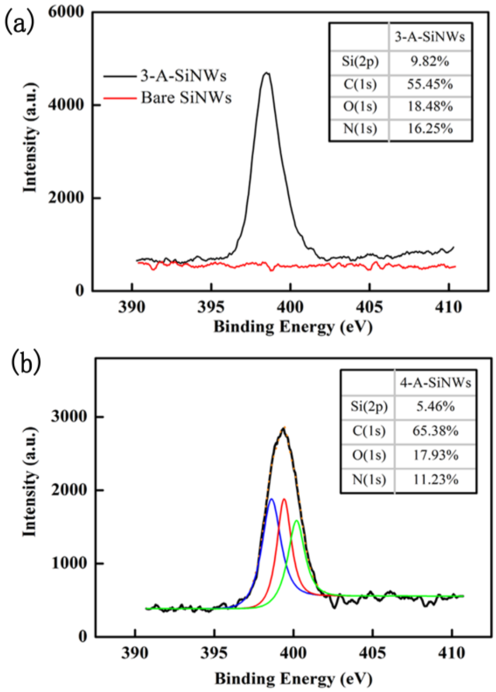


Fig. 3 XPS spectra of N1s region (a) Bare SiNWs and 3-A-SiNWs (b) 4-A-SiNWs Inset: the Relative atomic percentage of elements on the surface of 3-A-SiNWs and 4-A-SiNWs.

Fluorescence response of 4-A-SiNWs to Cu^{2+}

In order to investigate the binding between 4-A-SiNWs and Cu^{2+}, the 4-A-SiNWs were dispersed into the HEPES-buffer to form a 50μg/mL suspended solution. After the Cu^{2+} 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 Cu^{2+} 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 Cu^{2+} concentration and finally reached at a plateau at around 14 μM. It reveals that the ligand-containing 4-A-SiNWs has bound with Cu^{2+} to form a 4-A-SiNWs/Cu^{2+} complex. The apparent binding constant K between the 4-A-SiNWs and Cu^{2+} was calculated to be 2.25×10^5 by using a Langmuir-type analysis and fluorescence titration data.[38] The fluorescence response of 4-A-SiNWs to other metals ions such as Ca^{2+}, Cd^{2+}, Mg^{2+}, Al^{3+}, Co^{2+}, Na^{+}, Hg^{2+}, Mn^{2+}, K^{+}, Ni^{2+}, Pb^{2+}, Zn^{2+} were also measured and the results were shown in Fig. S1. From Fig. S1, it can be found that Cu^{2+} exhibited the most excellent fluorescence quenching character.

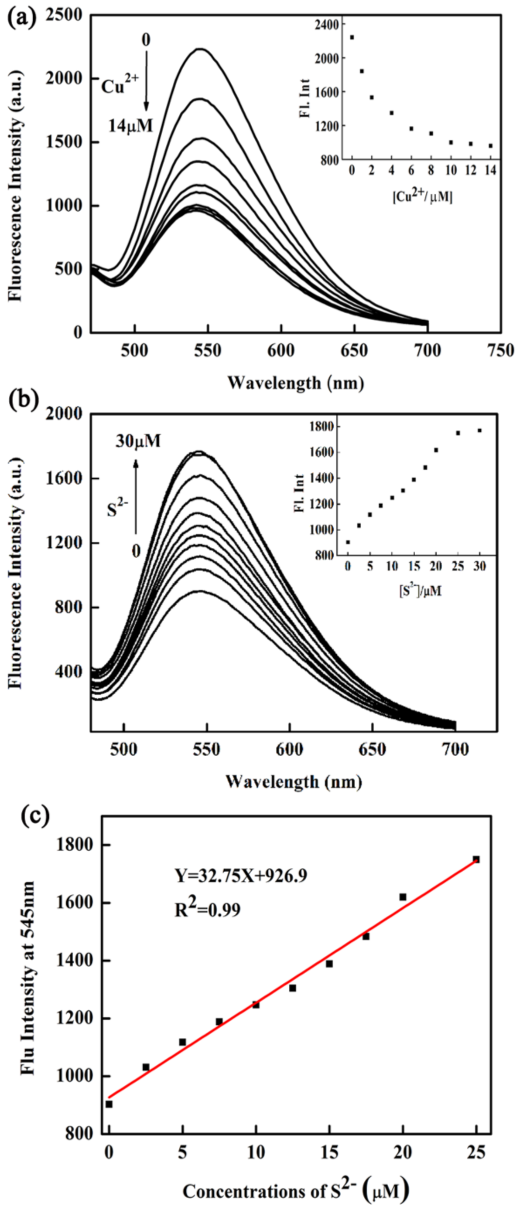
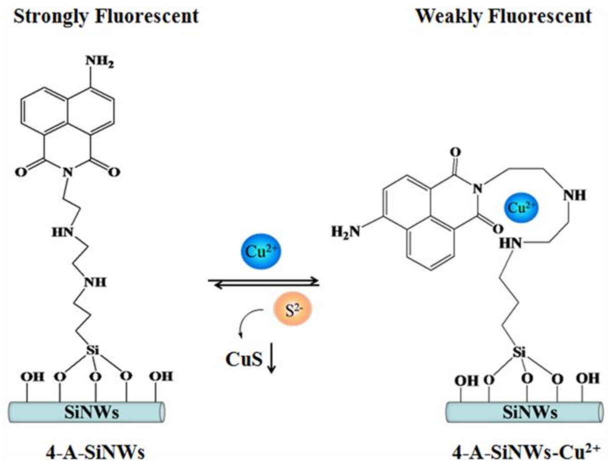


Fig. 4 Fluorescence response of (a) the 4-A-SiNWs (50μg/mL) in the presence of different concentrations of Cu^{2+} (0-14μM) (b) the 4-A-SiNWs/Cu^{2+} complex system (the 4-A-SiNWs: 50μg/mL, and Cu^{2+}: 10μM) in the presence of different concentrations of S^{2-} (0-30μM) in HEPES buffer (pH=7.0, 20mM). The insets in (a) and (b) show the fluorescence change at 545nm as a function of [Cu^{2+}] and [S^{2-}],respectively, λ_{ex}= 430nm. (c) The linear relationship between the fluorescence intensity and the S^{2-} concentration in the range of 0-25μM.

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

To check the response of the 4-A-SiNWs/Cu^{2+} complex to S^{2-}, the 4-A-SiNWs was preincubated with Cu^{2+}, and then the fluorescence response of the 4-A-SiNWs/Cu^{2+} complex to S^{2-} was investigated after adding S^{2-} instantly. As shown in Fig. 4b, the fluorescence of the 4-A-SiNWs/Cu^{2+} complex system was enhanced gradually with the increase of the S^{2-} concentration, indicating the 4-A-SiNWs/Cu^{2+} complex could be a promising fluorescent turn-on sensor for S^{2-}. The dependence of the emission intensity at 545nm on the S^{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^{2+} complex for the determination of S^{2-} was calculated to 0.88μM.

Scheme 2 illustrates the proposed response mechanism of the S^{2-} sensor. The paramagnetic Cu^{2+} can bind with the ligand-containing 4-A-SiNWs to form a 4-A-SiNWs/Cu^{2+} complex, which would lead to the fluorescence quenching of the system. The S^{2-} added into the 4-A-SiNWs/Cu^{2+} complex system could coordinate with the Cu^{2+} to form the stable species CuS (K_{sp}=3.63 x 10^{-36}), which resulted in the revival of the fluorescence.



Scheme 2 Proposed response mechanism of the S^{2-} sensor.

To investigate the selectivity, the fluorescence response of the 4-A-SiNWs/Cu^{2+} complex toward the common anions in environment was investigated. As shown in Fig. 5a, addition of 1mM F^{-}, Br^{-}, Cl^{-}, I^{-}, NO_3^{-}, HSO_3^{-}, CO_3^{2-}, CH_3COO^{-}, PO_4^{3-}, SO_3^{2-}, NO_2^{-}, SCN^{-}, $S_2O_3^{2-}$, SO_4^{2-} had little effect on the fluorescence emission from the sensing system. In contrast, addition of 30μM S^{2-} to the 4-A-SiNWs/Cu^{2+} system resulted in the obvious fluorescence enhancement. Furthermore, the fluorescence response of the 4-A-SiNWs/Cu^{2+} complex towards S^{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^{2-}. The results demonstrate that the 4-A-SiNWs/Cu^{2+} complex have sufficient selectivity for S^{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^{2-} were relatively stable in the pH range from 6 to 10. This result indicates that the current sensor can be used for S^{2-} monitoring in a wide pH range.

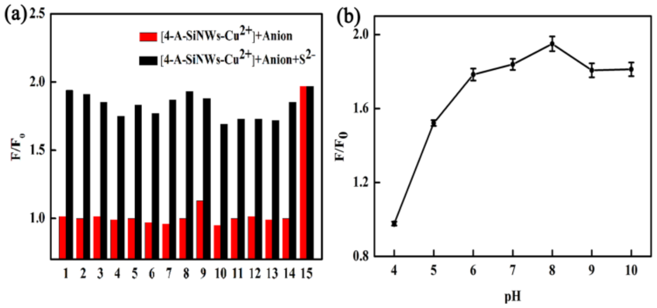


Fig. 5 (a) Fluorescence response of 4-A-SiNWs/Cu^{2+} complex (the 4-A-SiNWs: 50µg/mL, and Cu^{2+}: 10µM) in the presence of various anions alone (S^{2-}: 30µM, other anions: 1mM) and interfering ions with S^{2-}, respectively in HEPES buffer (pH=7.0 20mM).λ_{ex}=430nm,λ_{em}=545nm. 1-15 is successively for F$^-$, Br$^-$, Cl$^-$, I$^-$, NO_3^-, HSO_3^-, CO_3^{2-}, CH_3COO^-, PO_4^{3-}, SO_3^{2-}, NO_2^-, SCN$^-$, $S_2O_3^{2-}$, SO_4^{2-} and S^{2-}. (b) The pH effects on the fluorescence intensity at 545nm of the 4-A-SiNWs/Cu^{2+} (4-A-SiNWs: 50µg/mL, Cu^{2+}: 10µM) toward S^{2-} (30µM).

To further evaluate the applicability of the SiNWs-based S^{2-} sensor in real sample, the fluorescent sensor was applied to determine the S^{2-} in running water. After the running water containing different concentrations of S^{2-} was added into the system, the fluorescence of the 4-A-SiNWs/Cu^{2+} 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 S^{2-} 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 S^{2-}. According to Word Health Organization, the maximum recommended S^{2-} 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.

Table 1 Determination of sulfide anion in running water.

Samples	Amount of sulfide anion		Recovery(%)	RSD(%)
	Added(M)	Found(M)		
Running Water	0	—	—	—
	5.0	5.11	102.2	0.90
	10.0	9.69	96.9	3.85
	15.0	14.35	95.7	4.19
	20.0	19.52	97.6	2.73

Fluorescence response of the highly portable SiNW arrays-based sensor device to S^{2-}

In order to explore the application of our SiNW arrays-based sensor for real-time and in-situ monitoring of S^{2-} in the determinand, the modified 4-A-SiNWs array was pre-incubated with Cu^{2+}, then the unreacted Cu^{2+} was washed with deionized water and the SiNW arrays-based sensor device for S^{2-} was obtained. The sensor device was immersed into 1mL running water, then different concentrations of S^{2-} were added into the system. The fluorescent images of the sensor device before and after being treated with 50µM and 100µM S^{2-} were recorded by a fluorescence microscopy and the results were shown in Fig. 6. As expected, the addition of different concentrations of S^{2-} 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 S^{2-} in environmental analysis after finely quantifying the response of the device. It is well known that S^{2-} is not stable in water and can be easily transformed into other substances like a more toxic gas H_2S, which is always produced in some specific working environment. Therefore, the response of the senor device to H_2S was also investigated. From Fig. S2, it was found that the fluorescence of the sensor device increased obviously after being treated with H_2S. This phenomenon implied the potential use of sensor device in monitoring of H_2S in the environment.

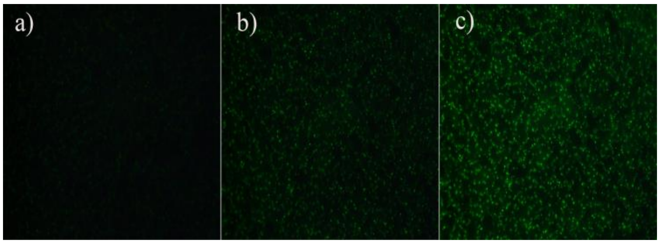


Fig. 6 Fluorescence images of the SiNW arrays-based sensor device (Cu^{2+} preincubated 4-A-SiNW arrays) before a) and after immersing in b) 50µM and c) 100µM S^{2-} for 0.5 minute.

Conclusions

In summary, we have designed and configured a rational fluorescent turn-on sensor for S^{2-} based on SiNWs and SiNW arrays. The present sensor displayed a good linear relationship between the fluorescence intensity and S^{2-} concentration from 0 to 25µM, and exhibited high selectivity for S^{2-} against other common anions. In addition, the present S^{2-} 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 S^{2-} at micromolar concentration in 100% aqueous solution. This work paves a way to fabricate the portable sensor device for S^{2-} and exhibits potential application in environmental analysis.

Acknowledgements

This work was supported by Chinese Academy of Sciences (Grant KGZD-EW-T02), NSFC (Grants 61025003, 51272302, 21103211, 51272258, 61204128 and 91333119) and National Basic Research Program of China (973 Program) (Grant 2012CB932400).

Notes and references

[a] *Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China Tel: +86-10-82543513, Fax: +86-10-82543513, Email:shiws@mail.ipc.ac.cn*
[b] *University of Chinese Academy of Sciences, Beijing 100190, China*

1. Hydrogen Sulfide, *Word Health Organization*, Geneva, 1981(Enviromental Health Criteria, 19).
2. R. F. Huang, X. W. Zheng and Y. J. Qu, *Anal. Chim. Acta*, 2007, 582, 267-274.
3. Gosselin, R. E.; Smith, R. P.; Hodge, H. C.; et al. *Clinical Toxicology of Commercial Products*, 5th ed.; Willians & Wilkins: Baltimore,MD, 1984; pp 198-202.
4. Patwardhan, S. A.; Abhyankar, S. M. *Colorrage*, 1988, 35, 15-18.
5. Balasubramanian, S.; Pugalenthi, V. *Water Res.*, 2000, 34, 4201-4206.
6. N. H. Bings, A. Bogaerts and J. A. C. Broekaert, *Anal. Chem.*, 2008, 80, 4317-4347.
7. M. Colon, J. L. Todolí M. Hidalgo and M. Iglesias, *Anal. Chim. Acta*, 2008, 609, 160-168.
8. N. S. Lawrence, R. P. Deo and J. Wang, *Anal. Chim. Acta*, 2004, 517, 131-137.
9. C. Giuriati, S. Cavalli, A. Gorni, D. Badocco and P. Pastore, *J. Chromatogr. A*, 2004, 1023, 105-112.
10. M. A. Spaziani, M. Tinani and M. K. Carroll, *Analyst*, 1997, 122, 1555-1557.
11. D. Jiménez, R. Martínez-Máñez, F. Sancenón, J. V. Ros-Lis, A. Benito and J. Soto, *J. Am. Chem. Soc.*, 2003, 125, 9000-9001.
12. X. F. Yang, L. P. Wang, H. Xu and M. L. Zhao, *Anal. Chim. Acta*, 2009, 631, 91-95.
13. C. R. Liu, J. Pan, S. Li, Y. Zhao, L. Y. Wu, C. E. Berkman, A. R. Whorton and M. Xian, *Angew. Chem., Int. Ed.*, 2011, 50, 10327-10329.
14. A. R. Lippert, E. J. New and C. J. Chang, *J. Am. Chem. Soc.*, 2011, 133, 10078-10080.
15. H. J. Peng, Y. F. Cheng, C. F. Dai, A. L. King, B. L. Predmore, D. J. Lefer and B. H. Wang, *Angew. Chem., Int. Ed.*, 2011, 50, 9672-9675.
16. Y. F. Zhu, D. H. Fan and W. Z. Shen, *J. Phys. Chem. C*, 2008, 112, 10402-10406.
17. K. Sasakura, K. Hanaoka, N. Shibuya, Y. Mikami, Y. Kimura, T. Komatsu, T. Ueno, T. Terai, H. Kimura and T. Nagano, *J. Am. Chem. Soc.*, 2011, 133, 18003-18005.
18. X. W. Cao, W. Y. Lin and L. W. He, *Org. Lett.*, 2011, 13, 4716-4719.
19. M. Q. Wang, K. Li, J. T. Hou, M. Y. Wu, Z. Huang and X. Q. Yu, *J. Org. Chem.*, 2012, 77, 8350-8354.
20. X. Y. Qu, C. J. Li, H. C. Chen, J. Mack, Z. Guo and Z. Shen, *Chem. Commun.*, 2013, 49, 7510-7512.
21. F. Y. Zheng, M. Wen, F. Zeng and S. Z.Wu, *Sens. Actuators, B*, 2013, 188, 1012-1018.
22. C. J. Gao, X. Liu, X. J. Jin, J. Wu, Y. J. Xie, W. S. Liu, X. J. Yao and Y. Tang, *Sens. Actuators, B*, 2013, 185, 125-131.
23. A. H. Gore, S. B. Vatre, P. V. Anbhule, S.-H. Han, S. R. Patil and G. B. Kolekar, *Analyst*, 2013, 138, 1329-1333.
24. X. F. Hou, F. Zeng, F. K. Du and S. Z. Wu, *Nanotechnology*, 2013, 24, 335502.
25. S. H. Lim, L. Feng, J. W. Kemling, C. J. Musto and K. S. Suslick, *Nat. Chem.*, 2009, 1, 562-567.
26. L. Feng, C. J. Musto, J. W. Kemling, S. H. Lim, W. Zhong and K. S. Suslick, *Anal. Chem.*, 2010, 82, 9433-9440.
27. I. Park, Z. Li, X. Li, A. P. Pisano and R. S. Williams, *Biosens. Bioelectron.*, 2007, 22, 2065-2070.
28. N. M. Iverson, P. W. Barone, M. Shandell, L. J. Trudel, S. Sen, F. Sen, V. Ivanov, E. Atolia, E. Farias, T. P. McNicholas, N. Reuel, N. M. A. Parry, G. N. Wogan and M. S. Strano, *Nat. Nano*, 2013, 8, 873-880.
29. S. W. Zeng, D. Baillargeat, H.-P. Ho and K.-T. Yong, *Chemical Society Reviews*, 2014, 43, 3426-3452.
30. W. Kim, J. K. Ng, M. E. Kunitake, B. R. Conklin and P. Yang, *J. Am. Chem. Soc.*, 2007, 129, 7228-7229.
31. G. F. Zheng, F. Patolsky, Y. Cui, W. U. Wang and C. M. Lieber, *Nat. Biotech.*, 2005, 23, 1294-1301.
32. J.-i. Hahm and C. M. Lieber, *Nano Lett.*, 2003, 4, 51-54.
33. W. S. Shi, H. Y. Peng, Y. F. Zheng, N. Wang, N. G. Shang, Z. W. Pan, C. S. Lee and S. T. Lee, *Adv.Mater.*, 2000, 12, 1343-1345.
34. K. Q. Peng, A. J. Lu, R. Zhang and S.-T. Lee, *Adv. Funct. Mater.*, 2008, 18, 3026-3035.
35. S. S. Tooru Yoshida, *Bull. Chem. Soc. Jpn.*, 1974, 47, 50-53.
36. C. m. Suspène, R. g. Barattin, C. Celle, A. Carella and J.-P. Simonato, *J. Phys. Chem. C*, 2010, 114, 3924-3931.
37. Z. Jin, X. B. Zhang, D. X. Xie, Y. J. Gong, J. Zhang, X. Chen, G. L. Shen and R.-Q. Yu, *Anal. Chem.*, 2010, 82, 6343-6346.
38. A. B. Descalzo, M. D. Marcos, R. Martinez-Manez, J. Soto, D. Beltran and P. Amoros, *J. Mater. Chem.*, 2005, 15, 2721-2731.