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ARTICLE

## A highly selective and sensitive resonance Rayleigh scattering sensor for sulfide ions detection using Ag<sub>2</sub>Te nanocrystals

Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Shuguang Yan<sup>ab</sup>, Rongcai Song<sup>a</sup>, Yangyang Li<sup>a</sup>, Yurong Tang,<sup>c\*</sup>

Ag<sub>2</sub>Te nanocrystals (NCs) Ag<sub>2</sub>Te nanocrystals (NCs) were prepared from inexpensive and environmentally friendly raw materials by a facile route using liquid precursors at low temperatures under atmospheric pressure. The as-prepared Ag<sub>2</sub>Te NCs have been characterized by UV-vis, TEM and XPS. We have demonstrated that the enhancement of resonance Rayleigh scattering (RRS) was observed when sulfide ions were injected into the prepared Ag<sub>2</sub>Te NCs through the interaction between sulfide ions and Ag<sub>2</sub>Te NCs. A result which leads to change in the conformation of the Ag<sub>2</sub>Te NCs and formed nanocomposite Ag<sub>2</sub>S/Ag<sub>2</sub>Te NCs was derived, and a novel RRS system for direct detection of sulfide was established. The possible enhancement RRS mechanism is discussed in this work. The resulting RRS sensor enables the detection of sulfide ions with limit of detection reaching 7.8 ng/mL (3σ/K) in a wide linear range from 0.026 μg/mL (10σ/K) to 9.87 μg/mL. The practicality of this probe for the detection of sulfide ions in urban river water samples has been validated and its advantages of simplicity, sensitivity, selectivity, and low cost have been demonstrated. The recovery of spiked sulfide ions in urban river water samples ranges from 96% to 103%. The relative standard deviation (RSD) for eleven replicate detections is 2.6%.

### Introduction

The conclusions section should come in this section at the end of the article, before the acknowledgements. Silver (Ag)-chalcogenide semiconductor NCs have attracted considerable interest owing to their distinctive properties including low toxic components and promising application of analysis chemistry<sup>1,2</sup>. By far many scientific issues with Ag<sub>2</sub>X (X=S, Se, Te) still await further study. Currently, a series of methods for synthesis Ag<sub>2</sub>X (X=S, Se, Te) NCs have been developed<sup>3-5</sup>, but high quality and one-step methodology for the construction of Ag<sub>2</sub>X (X=S, Se, Te) on multitudinous is still a challenge in this field, and all of these strategies depend on the high-temperature organometallic routes that require complex precursors and stringent reaction conditions<sup>6,7</sup>. In addition, the as-prepared of NCs in organic phase need to be further solubilized in aqueous solution where NCs stability would be drastically decreased. Aqueous NCs synthesis represents an alternative strategy to the conventional organometallic strategies and has been widely applied to prepare Cd-chalcogenide NCs emitting in the visible region<sup>8</sup>. Proverbially, Aqueous NCs synthesis can be conducted under mild

conditions and is much more straightforward<sup>9</sup>. Moreover, the NCs prepared via aqueous synthesis are in general water-soluble, stable, and small in hydrodynamic size, which are superior properties for bioimaging applications. Therefore, a much-simplified and robust synthetic strategy to prepare Ag<sub>2</sub>X (X=S, Se, Te) NCs with water-solubility and stability is highly urgent needed.

Sulfide is extensively present in both natural water through bacterial immobilization of sulfur-containing compounds and wastewater mainly caused by many of the manufacturing process<sup>10</sup>. Sulfide salts may also be added to industrial waste streams in order to control the levels of poisonous heavy metal ions<sup>11</sup>. Hence, its concentration needs to be controlled. Thus, the detection of sulfide has gained importance within the analytical community as a consequence of the poisonous of hydrogen sulfide<sup>12</sup> and the corresponding risks associated with exposure in a large amount of occupational field. Several methods have been applied to the detection of sulfide, for example, electrochemistry<sup>13</sup>, chromatography<sup>14</sup> and spectroscopy<sup>15,16</sup>. However, these methods often require time-consuming analysis, complicated procedures, large sample volumes, and/or specialized skills. Alternatively, various probe systems for the detection of sulfide have been developed on the basis of analytes induced signal changes through their interactions with metal ions and nanomaterial such as Cu NCs<sup>17</sup>, Au/Ag NCs<sup>18</sup>, PbO/SiO<sub>2</sub> nanocomposite<sup>19</sup> and Cu/Au nanoparticle<sup>20</sup>. These probe systems are poor sensitivity and selective and high costs are still problematic. Thus, there is a need for sensitive and selective probes for the detection of sulfide.

<sup>a</sup> College of Energy Resources, Chengdu University of Technology, Chengdu, sichuan 610059, China.

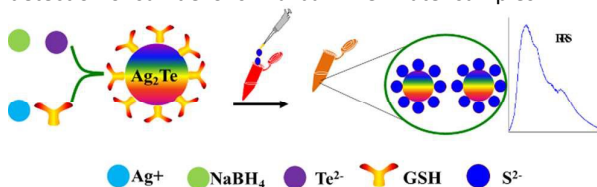
<sup>b</sup> Key Laboratory of Green Chemistry & Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu, Sichuan 610064, China. Analytical & Testing Center, Sichuan University, Chengdu, Sichuan 610064, China.

<sup>c</sup> College of Material and Chemistry & Chemical Engineering, Chengdu University of Technology, Chengdu 610059, China.

\*Corresponding author, Tel& Fax+86-28-8407-9005, E-mail: tangyurong@163.com

It is well known that resonance Rayleigh scattering (RRS) for its simplicity, rapidity and sensitivity as an analytical approach developed in recent decades<sup>21</sup>. RRS is a special elastic scattering generated when the wavelength of Rayleigh scattering is located at or close to the molecular absorption band<sup>22</sup>. The intensity of RRS would rapidly increase when the wavelength of the incident beam is close to that of the absorption band of the aggregation<sup>23</sup>. RRS is very sensitive to the weak interaction between different molecules and the aggregation interaction of molecules<sup>24</sup>. This technique has been applied successfully to studying biological macromolecules<sup>25, 26</sup>, some metal ions<sup>27</sup>, trace amounts of inorganic ions<sup>28</sup> and physicochemical constants<sup>29</sup>. The spectral characteristics and scattering intensity are strongly influenced by the molecular size, shape, conformation, and interfacial properties<sup>30</sup>. In particular, with the rapid development of nanotechnology, great attention has been focused on the using of nanoparticles as the RRS probes.

Herein, we developed a facile one-step aqueous synthesis of Ag<sub>2</sub>Te NCs from AgNO<sub>3</sub>, NaBH<sub>4</sub> and Te powder in the presence of GSH as a stabilizer. Interestingly, sulfide anion diffuses to react with Ag<sup>+</sup> on the surface of Ag<sub>2</sub>Te NCs when sulfide anion was injected into the prepared Ag<sub>2</sub>Te NCs. Accompanied by an increase in the RRS of Ag<sub>2</sub>Te NCs, it can be used to develop a chemical sensor for the detection of sulfide anion with high sensitivity and selectivity. In this RRS process, Ag<sub>2</sub>Te NCs and sulfide anion display weak RRS. The nanocomposite of Ag<sub>2</sub>S/Ag<sub>2</sub>Te is formed when Ag<sub>2</sub>Te NCs interact with sulfide anion and enhance the RRS of the Ag<sub>2</sub>Te NCs (Scheme 1). To our knowledge, a sensitive and selective method for the detection of S<sup>2-</sup> for the first time with RRS was reported. We further validated the practicality of this probe through the detection of sulfide ions in urban river water samples.



**Scheme 1** Schematic Representation of the operation of the Ag<sub>2</sub>Te NCs Probe for the Detection of S<sup>2-</sup>.

## Experimental Section

### Reagents

AgNO<sub>3</sub> (99%) was purchased from Shanghai Chemicals Reagent Co., Shanghai. Tellurium powder (99.999%) and Glutathione (98%) was purchased from Aladdin Industrial Co., Shanghai. All other reagents were used of analytical reagent grade without further purification and deionized water with conductivity of 18.2 MΩcm<sup>-1</sup> was used in this experiment from a water purification system (ULUPURE, Chengdu, China).

### Instrumentations

Transmission electron microscopy (TEM) of Ag<sub>2</sub>Te NCs were carried out on a Tecnai G2 F20 S-TWIN transmission electron microscope at an accelerating voltage of 200 kV (FEI Co.,

America). X-ray photoelectron spectroscopy (XPS) was performed with a XSAM 800 electron spectrometer (Kratos) using monochromatic Al Kα radiation for the analysis of the surface composition and chemical states of the product. The UV-vis spectra and RRS spectra were obtained with a U-2910 UV-vis spectrophotometer and an F-7000 fluorescence spectrophotometer (Hitachi Co., Tokyo, Japan).

### Preparation of GSH-Ag<sub>2</sub>Te NCs

Aqueous colloids GSH-Ag<sub>2</sub>Te NCs solution was prepared at low temperature according to the reference<sup>1</sup>. It was described in detail as follows: Under N<sub>2</sub> atmosphere, deionized water (10 mL) was added to Te powder (0.1 mmol) and excessive NaBH<sub>4</sub> under magnetic stirring at room temperature. After about 2 h, the colorless solution of NaHTe was prepared.

0.4 mmol AgNO<sub>3</sub> was dissolved in 150 mL of deionized water and 0.4 mmol of GSH was added under stirring, followed by adjusting to pH = 13 by dropwise addition of 1.0 mol/L NaOH solution. The solution was placed in a tree-necked flask and deaerated by N<sub>2</sub> bubbling for about 30 min. Under magnetic stirring, 0.1 mmol H<sub>2</sub>Te gas generated by the reaction of the solution of NaHTe with diluted HCl (1 mol/L) was passed through the oxygen-free original solution together with a slow nitrogen flow for 10 min. Ag<sub>2</sub>Te NCs precursors were formed at this stage. The molar ratio of Te/Ag<sup>+</sup>/GSH was fixed at 1:4:4. Then the resulting mixture was subjected to reflux at 85 °C for 1 h under oxygen-free condition with condenser. Ag<sub>2</sub>Te NCs were obtained. The concentration of Ag<sub>2</sub>Te NCs was 6.67×10<sup>-3</sup> mol/L (determined by the Te<sup>2-</sup> concentration)<sup>31</sup>.

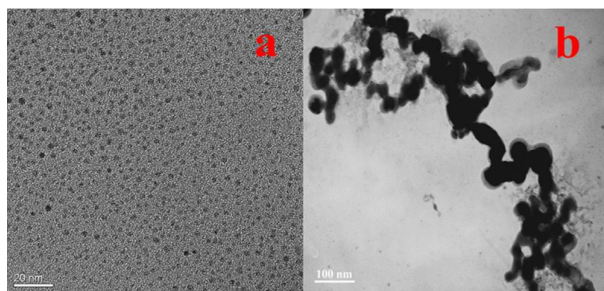
### Experimental procedure

60 μL above prepared GSH-Ag<sub>2</sub>Te NCs, 100 μL 0.1 mol NaOH-EDTA buffer and appropriate amounts of sulfide anion were added into a 2 mL colorimetric tube, then diluted with deionized water to the mark and mixed thoroughly with gentle shake. After incubated for 10 min, the RRS spectra were recorded with synchronous scanning at λ<sub>ex</sub> = λ<sub>em</sub> and RRS intensity for complexes and R<sub>0</sub> for reagent blank were measured at their own maximum wavelengths, The UV-vis absorption spectra of solution were also examined.

## Results and Discussion

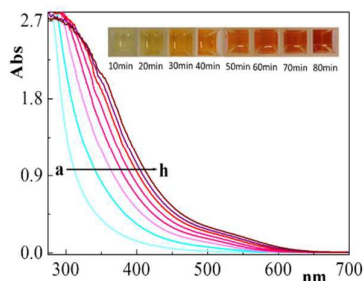
### GSH-Ag<sub>2</sub>Te NCs Characterization

The strategy for synthesizing GSH-Ag<sub>2</sub>Te NCs is based on a colloidal chemical synthetic approach. The details on the synthesis of Ag<sub>2</sub>Te NCs were addressed in the experimental section and this synthetic approach produced nearly monodispersed Ag<sub>2</sub>Te NCs (see transmission electron microscopy (TEM) images in Fig. 1) with a uniform diameter of

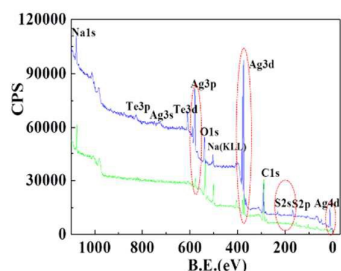


**Fig. 1** (a) TEM images of  $\text{Ag}_2\text{Te}$  NCs. (b) TEM images of  $\text{Ag}_2\text{Te}$  NCs- $\text{S}^{2-}$  system. Insert figure 1b, HRTEM images of  $\text{Ag}_2\text{Te}$  NCs- $\text{S}^{2-}$  system.

2 nm. Heating of mixture solution of  $\text{Ag}_2\text{Te}$  NCs results in a gradually red shift of the maximum absorption of the solution system (Fig. 2), which implies that  $\text{Ag}_2\text{Te}$  NCs is slowly growing in situ on the  $\text{Ag}_2\text{Te}$  NCs core. With the reflux proceeding, the excitonic absorption peak of nanoparticles shifts to the longer wavelengths (lower energies) as the NCs grow to larger size. This result is agreed with the consequence of the quantum confinement effect<sup>32</sup>. X-ray photoelectron spectroscopy (XPS) was used to analyze the surface composition of the as-prepared products. The survey-scan and narrow-scan spectra of the  $\text{Ag}_{3d}$  are shown in Fig. 3. The binding energy XPS data were referenced to the  $\text{C}_{1s}$  of aliphatic carbon at 284.9 eV. The peaks at 367.56 and 373.59 eV correspond to  $\text{Ag}_{3d}$ , and the peak at 161.4 eV corresponds to  $\text{S}_{2p}$ . Fig. 3b showed XPS pattern of  $\text{Ag}_2\text{S}/\text{Ag}_2\text{Te}$  nanocomposite when sulfide anion was added  $\text{Ag}_2\text{Te}$  NCs and adsorbed on the surface of the NCs. It can be seen that the peak strength of sulfide anions on the surface of  $\text{Ag}_2\text{S}/\text{Ag}_2\text{Te}$  nanocomposite is stronger than  $\text{Ag}_2\text{Te}$  NCs.

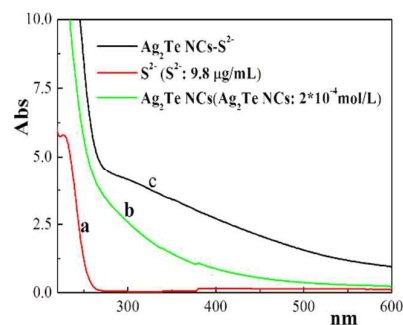


**Fig. 2** UV-vis spectra of  $\text{Ag}_2\text{Te}$  NCs at different growth times. a-h: 10 min, 20 min, 30 min, 40 min, 50 min, 60 min, 70 min, 80 min, respectively.

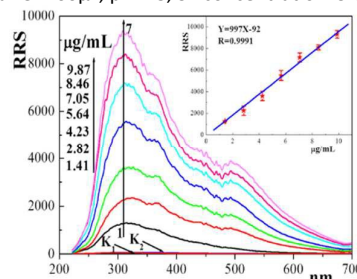


**Fig. 3** XPS pattern of  $\text{Ag}_2\text{Te}$  NCs and  $\text{Ag}_2\text{S}/\text{Ag}_2\text{Te}$  nanocomposite  
**UV-vis absorption and RRS spectra of interaction between  $\text{Ag}_2\text{Te}$  NCs and sulfide anion**

UV-vis absorption measurement is a very simple method and applicable to explore the structural change and to know the complex formation. The interaction between  $\text{Ag}_2\text{Te}$  NCs and sulfide anion was investigated by UV-vis absorption spectra. As shown in Fig. 4, absorption band Fig. 4a and Fig. 4b are assigned for sulfide anion and  $\text{Ag}_2\text{Te}$  NCs. And a new band was observed (Fig. 4c) when the sulfide anion was added into the  $\text{Ag}_2\text{Te}$  NCs solution. The results indicated that it may be formed aggregation nanoparticle between  $\text{Ag}_2\text{Te}$  NCs and sulfide anion, which indicates that there are strong interaction between  $\text{Ag}_2\text{Te}$  NCs and sulfide anion. From the RRS spectra (Fig. 5) of  $\text{Ag}_2\text{Te}$  NCs-sulfide anion it can be seen that the RRS intensity of sulfide anion solution is very weak and the maximum scattering peak is located at 259 nm. Besides, the RRS intensity of  $\text{Ag}_2\text{Te}$  NCs is very weak and the maximum scattering peak is located at 305 nm. Furthermore, when  $\text{Ag}_2\text{Te}$  NCs reacted with sulfide anion solution, the RRS intensity of the system can be greatly enhanced and a new RRS spectrum appears, and the maximum scattering peak is locked at 310 nm. At the same time, the enhancement of RRS intensity was in proportion to the concentration of sulfide anion.



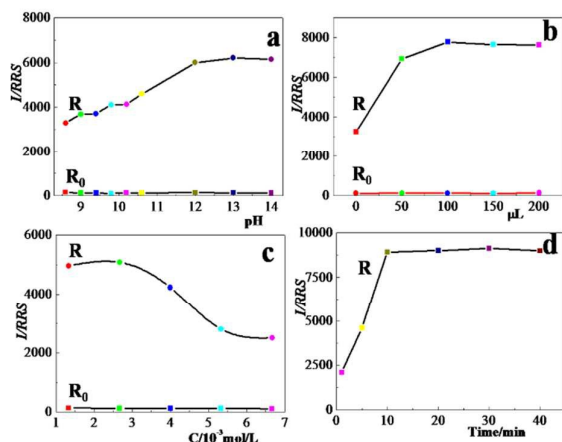
**Fig. 4** UV-vis spectra of (a)  $\text{Ag}_2\text{Te}$  NCs, (b)  $\text{S}^{2-}$  and (c)  $\text{Ag}_2\text{Te}$  NCs in the presence of  $\text{S}^{2-}$  ( $\text{Ag}_2\text{Te}$  NCs as reference).  $\text{Ag}_2\text{Te}$  NCs,  $2 \times 10^{-4}$  mol/L; NaOH-EDTA buffer 100  $\mu\text{L}$ , pH=13,  $\text{S}^{2-}$  concentration: 9.87  $\mu\text{g}/\text{mL}$ .



**Fig. 5** Validation of the use of  $\text{Ag}_2\text{Te}$  NCs as probe for the detection of  $\text{S}^{2-}$ .  $k_1$ :  $\text{Ag}_2\text{Te}$  NCs ( $\text{Ag}_2\text{Te}$  NCs concentration:  $2 \times 10^{-4}$  mol/L),  $k_2$ :  $\text{S}^{2-}$  ( $\text{S}^{2-}$  concentration: 9.87  $\mu\text{g}/\text{mL}$ ), The concentrations of  $\text{S}^{2-}$ : 1.41, 2.82, 4.23, 5.64, 7.05, 8.46, 9.87  $\mu\text{g}/\text{mL}$ , respectively. pH=13 NaOH-EDTA buffer 100  $\mu\text{L}$ . Each data is obtained from three determinations.

**Optimization conditions of the  $\text{Ag}_2\text{Te}$  NCs-sulfide anion system**





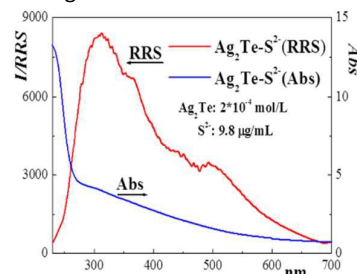
**Fig.6** a: The effect of pH on RRS intensities. Ag<sub>2</sub>Te NCs 2×10<sup>-4</sup> mol/L; NaOH-EDTA buffer 100 μL; S<sup>2-</sup> 7 μg/mL. b: The effect of amount of NaOH-EDTA buffer on RRS intensities. Ag<sub>2</sub>Te NCs, 2×10<sup>-4</sup> mol/L; pH=13, S<sup>2-</sup> 7 μg/mL. c: The effect of Ag<sub>2</sub>Te NCs concentration on RRS intensities. NaOH-EDTA buffer 100 μL; pH=13.0; S<sup>2-</sup> 7 μg/mL. d: The time-dependent RRS of the system after addition of S<sup>2-</sup>. Ag<sub>2</sub>Te NCs, 2×10<sup>-4</sup> mol/L; pH=13; NaOH-EDTA buffer 100 μL; S<sup>2-</sup> 9.8 μg/mL. R: Ag<sub>2</sub>Te NCs- S<sup>2-</sup> system, R<sub>0</sub>: blank.

We investigated the role that pH played in determining the selectivity of the Ag<sub>2</sub>Te NCs toward sulfide anion. The results indicated that 0.1 mol/L NaOH-EDTA (pH=13) was the best buffer solution of the reaction system. Therefore, in this case, pH=13 was chosen as the optimal reaction acidity. The suitable amount of buffer solution for Ag<sub>2</sub>Te NCs-sulfide anion system was 50-200 μL. The selected amounts of buffer solution were 100 μL. Besides, the effect of concentration of Ag<sub>2</sub>Te NCs was studied. The results showed that the optimum amount of Ag<sub>2</sub>Te NCs was 60 μL for the determination of sulfide anion. The concentration of Ag<sub>2</sub>Te NCs was 2×10<sup>-4</sup> mol/L. Furthermore, the effect of incubation time on RRS intensity was investigated. The RRS of Ag<sub>2</sub>Te NCs increased quickly in the presence of sulfide anion, and reached stability in 10 min. therefore, the RRS spectra were recorded after 10 min when the reaction has been completed.

**The interaction between Ag<sub>2</sub>Te NCs and sulfide anion and the enhancement reasons of RRS**

The aggregation nanoparticle of Ag<sub>2</sub>S/Ag<sub>2</sub>Te is formed between Ag<sub>2</sub>Te NCs and sulfide anion and enhanced of the RRS of the Ag<sub>2</sub>Te NCs. In the process of synthesis Ag<sub>2</sub>Te NCs, a large amount of GSH can self-assemble on the surface of Ag<sub>2</sub>Te NCs to form negatively charged supermolecules and Ag<sub>2</sub>Te NCs have good water solubility. Besides, the TEM analysis results show that Ag<sub>2</sub>Te NCs have unique monodispersed. Importantly, there are many Ag<sup>+</sup> on the surface of Ag<sub>2</sub>Te NCs. In strong alkaline media, Ag<sup>+</sup> on the surface of the NCs reacts with sulfide anion and forms Ag<sub>2</sub>S, which aggregates larger nanocomposites of Ag<sub>2</sub>S/Ag<sub>2</sub>Te with the small Ag<sub>2</sub>Te NCs and leads to the RRS intensity at 310 nm increasing, when sulfide anion was added to Ag<sub>2</sub>Te NCs and adsorbed on the surface of the NCs. It is proved by the XPS pattern of Fig. 3b and RRS spectra of Fig. 5. Accordingly, a simple and rapid RRS method can be developed to measure sulfide anion.

RRS is an absorption-rescattering process produced by the resonance between the Rayleigh scattering and the light absorption with the same frequency when the wavelength of Rayleigh scattering is located at its absorption band<sup>33</sup>. Therefore, RRS spectrum is closely related to the absorption spectrum. From Fig. 7 it can be seen that the RRS peak of Ag<sub>2</sub>S/Ag<sub>2</sub>Te nanocomposite at 310 nm are close to the absorption band, which would result in the resonance enhanced scattering.



**Fig. 7** The comparison of UV-vis absorption spectrum with corrected RRS spectrum. (Abs) UV-vis absorption spectrum. (RRS) RRS spectrum. Ag<sub>2</sub>Te NCs concentration: 2.0×10<sup>-4</sup> mol/L, S<sup>2-</sup> concentration: 9.87 μg/mL.

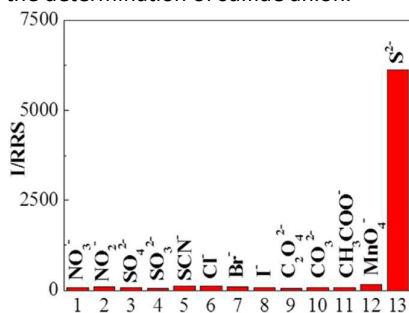
A more important reason for the enhanced RRS is hydrophobic effect. Large amounts of GSH can self-assemble on the surface of Ag<sub>2</sub>Te NCs to form negatively charged supermolecules and Ag<sub>2</sub>Te NCs have good water solubility, therefore, the RRS intensity of NCs and sulfide anion are all very weak. It can be speculated that when they combine with each other to form Ag<sub>2</sub>S on the surface of Ag<sub>2</sub>Te NCs, Ag<sub>2</sub>S shell grows in situ on the Ag<sub>2</sub>Te NCs core, which causes the increase of the hydrophobicity of the nanocomposite. The liquid-solid interface between the Ag<sub>2</sub>S/Ag<sub>2</sub>Te nanocomposite and water may be formed and produces surface enhanced scattering and enhances the scattering intensities<sup>34</sup>. A sketch of the combination is shown in scheme 1.

The last but not the least reason for the enhanced RRS is increase of the molecular volume. It is easy for sulfide anion to bind on to the surface of Ag<sub>2</sub>Te NCs via the electrovalent bond of S-Ag, which resulted in the increase of the diameter up from about 2-3 nm to about 30-50 nm. With the increased amount of the Ag<sub>2</sub>S aggregated on the surface of Ag<sub>2</sub>Te NCs, the volume of Ag<sub>2</sub>S/Ag<sub>2</sub>Te nanocomposite would gradually increase owing to grow of the Ag<sub>2</sub>S. Thus, the increase of the molecular volume is one of the reasons for the RRS enhancement<sup>35</sup>. It is proved by the TEM image of Fig. 1b and RRS spectra of Fig. 5.

**Sensitivity and Selectivity**

The RRS at 310 nm of the Ag<sub>2</sub>Te NCs-sulfide anion system increased upon increasing the concentration of sulfide anion from 0 to 9.87 μg/mL. The regression equation is I=997C-92. The linear region was obtained in the plots of the value of I<sub>RRS</sub> versus the concentrations of sulfide anion from 0.026 μg/mL to 9.87 μg/mL (Fig. 5). The correlation coefficient (R) of the linear plot was 0.9991. The LOD of Ag<sub>2</sub>Te NCs for sulfide anion was 7.8 ng/mL.

The selectivity of the  $\text{Ag}_2\text{Te}$  NCs probe toward sulfide anion ( $7 \mu\text{g/mL}$ ) against one of the following ions and their corresponding species was tested ( $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{SCN}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{MnO}_4^-$ ,  $\text{EDTA}^{2-}$ ,  $\text{OH}^-$ ). The results are shown in Fig. 8. The larger amounts of common inorganic, acid radical ions did not interfere with determination. Therefore, the RRS method has a good selectivity and can be applied to the determination of sulfide anion.



**Fig. 8** Relative RRS intensity of  $\text{Ag}_2\text{Te}$  NCs probe in NaOH-EDTA buffer solution ( $0.1 \text{ mol/L}$ ,  $\text{pH}=13$ ) in the presence of anions with the addition of a masking reagent. The concentrations of  $\text{S}^{2-}$  and each of the other anions were  $7 \mu\text{g/mL}$  and  $500 \mu\text{g/mL}$ , respectively.

#### Detection of sulfide anion in urban river water samples

To further test the possibility of the  $\text{Ag}_2\text{Te}$  NCs probe for the sulfide anion in real samples, we applied the  $\text{Ag}_2\text{Te}$  NCs probe to determine the concentrations of sulfide anion in urban river water samples. We chose the urban river water sample, mainly because sulfide anion will pollute the drinking water when the water contained high concentrations of sulfide anion. The urban river water samples were treated and all kind of solid particles in the urban river water samples were filtrated used  $0.2 \mu\text{m}$  filtration membrane. Table 1 collects the results for the RRS determinations of sulfide anion. Therefore, the described RRS method was applied for determination of sulfide anion based on the  $\text{Ag}_2\text{Te}$  NCs as RRS probe under the optimal conditions. These values indicated that this method had good accuracy for quantities determination of sulfide ion in urban river water sample.

**Table 1** Analytical results for sulfide anion in urban river water samples.

Sample	Found ( $\mu\text{g/mL}$ )	Added ( $\mu\text{g/mL}$ )	Total found ( $\mu\text{g/mL}$ ) ( $n=5$ )	Recovery (%)
Sample 1	ND	2.62	2.54	96%
Sample 2	ND	3.93	3.87	98%
Sample 3	ND	5.24	5.41	103%

ND: no found

**Table 2** Comparison of the proposed method with some methods recently reported in literature.

System	pH	D.L.	L.R.	R.S.D (%)	Ref.
NPs/Colorimetric	-	50 nM	50 nM–100 $\mu\text{M}$	-	16
NCs/Fluorescent	5.0	0.83 nM	0.01–9 $\mu\text{M}$	-	18
Phosphorescence	-	0.138 $\mu\text{M}$	2.67–596 $\mu\text{M}$	1.82	19
Colorimetric	5.2	0.3 $\mu\text{M}$	0–1.5 $\mu\text{M}$	-	20
Ion chromatography	7.4	$2.5 \times 10^{-6} \text{ mol/L}$	$1.0 \times 10^{-5}$ – $1.0 \times 10^{-3} \text{ mol/L}$	3.9	36
GC-MS	9.3	$10^{-6} \text{ mol/L}$	$1.0 \times 10^{-5}$ – $1.0 \times 10^{-4} \text{ mol/L}$	2.7	37
VG-ICP-QMS	-	$<1.0 \times 10^{-3} \mu\text{g/mL}$	$1.0 \times 10^{-2}$ – $1.0 \times 10^{-1} \mu\text{g/mL}$	0.4–1.3	38
Optode	7.0	$2.4 \times 10^{-3} \text{ mol/L}$	$2.5 \times 10^{-3}$ – $2.8 \times 10^{-2} \text{ mol/L}$	2.0	39

SPE	6.5	0.3 $\mu\text{M}$	1.09–16.3 $\mu\text{M}$	3.2	40
NCs/RRS	13	7.8 ng/mL	0.026–9.87 $\mu\text{g/mL}$	2.6	This work

## Conclusions

We prepared  $\text{Ag}_2\text{Te}$  NCs from inexpensive and environmentally friendly raw materials by a straightforward approach using liquid precursors at low temperatures under atmospheric pressure. They are much stable in aqueous solution media. This synthetic approach produced nearly monodispersed  $\text{Ag}_2\text{Te}$  NCs that allow sensitive (LOD:  $7.8 \text{ ng/mL}$ ) and selective detection of sulfide anion through RRS. A comparison between the figures of merit of  $\text{Ag}_2\text{Te}$  NCs probe with those of the previously reported ones (Table 2) clearly revealed that this RRS sensor can be categorized among the good sulfide probe ever reported. The interaction mechanism between  $\text{Ag}_2\text{Te}$  NCs and sulfide anion was investigated and the reasons of RRS enhancement were discussed. From the discussion it can be concluded that  $\text{Ag}_2\text{S}/\text{Ag}_2\text{Te}$  nanocomposites was formed when sulfide anion was added into the  $\text{Ag}_2\text{Te}$  NCs solution. The  $\text{Ag}_2\text{Te}$  NCs probe allows detection of sulfide anion in urban river water samples without tedious sample pretreatment processes. A new strategy of the study purposes not only for the direct sulfide anion determination but also the sensor that might indirectly monitor the activity of bacteria, which could produce hydrogen sulfide. It will provide a new strategy for the research of those bacteria in the field of biology. With RRS technique widely available in various biological substances, developments of similar nanocrystals RRS sensing strategies can be expected to detect other molecules for chemical and biological applications.

## Acknowledgements

Authors gratefully acknowledge financial support for this project from the National Natural Science Foundation of China [Grants 21375089 and 21105067]. The authors also would like to show gratitude for Dr. Shanlin Wang at Analytical & Testing Center of Sichuan University for her assistance in the TEM analysis.

## Notes and references

The authors declare no competing financial interest.

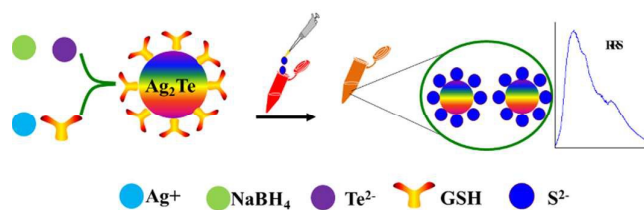
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## Graphical Abstract



Schematic Representation of the operation of the Ag<sub>2</sub>Te NCs Probe for the Detection of S<sup>2-</sup>