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A colorimetric Boolean INHIBIT logic gate for the determination of sulfide based on citrate-capped gold nanoparticles

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Abstract

Herein, we designed a noncommutative logic gate (INHIBIT gate) by utilizing citrate-capped AuNPs as a signal transducer and S^{2-} and TU as mechanical activators and devised a colorimetric sensor for inexpensive, label-free, rapid, sensitive and selective determination of S^{2-}. Under the optimum conditions, 4 μM S^{2-} could induce a significant color change which can be directly recognized by naked eyes. The calibration curve for the absorbance ratios of A_{680}/A_{520} against S^{2-} concentration was linear in the range from 2 to 9 μM and the RSD was 1.3% for the determination of 4 μM S^{2-} (n=6). Moreover, this logic gate was successfully applied for sensing S^{2-} in various practical samples, implying its wide applications in food, environment, and biological system.

Introduction

Inorganic anions are ubiquitous in biological systems and play vital roles in industrial, medical, and environmental processes. The design of sensitive and selective probes has long been a focus of research as it can provide on-site, real-time detection and quantification of beneficial and toxic anions. Sulfide (S^{2-}) is an inorganic anion widely present in both natural and waste waters, and it is very detrimental to environment attributed to the releasing of hydrogen sulfide (H_2S), which is a toxic gas with a characteristic malodor of rotten eggs. However, H_2S is of high medical concern recently since it has been demonstrated to be an endogenously produced gaseous signaling molecule other than nitric oxide and carbon monoxide. H_2S can interact directly with downstream protein targets through post-translational cysteine sulfhydration as well as via binding to heme iron centers.[1, 2] Furthermore, researches have indicated that the H_2S level is altered in some diseases, such as Alzheimer's disease and Down's syndrome.[3, 4] Although several strategies have been documented for determining sulfide in the literature,[5-14] the design of new sensors for sulfide in food chemistry, ecosystem, and biological system is still appealing.

In recent years, molecular Boolean logic gates have been extensively studied. Application of logic gates in sensing or biosensing simplify the results of

measurement, leaving the determination of analytes in samples either "have" or "none", or the diagnosis of disease either "yes" or "no". In this field, colorimetric logic gates based on the high absorption extinction coefficients and strongly distance-dependent optical properties of gold nanoparticles (AuNPs) have become more and more attractive for point-of-use application due to their sensitivity, rapidness, low-cost and especially ease of readout with naked eye. Up to now, various AuNPs-based colorimetric logic gates, such as AND, OR, NOR, and INHIBIT, have been established on the platform of DNAzyme,[15, 16] aptamer,[17-20] and target-ligand coordination.[21-23] The inputs of most logic gates reported previously have been (bio)molecules and metal ions. However, small anions implemented as input in the design of AuNPs-based colorimetric logic gates are exceedingly scarce.[24] Herein, we developed a Boolean logic gate based on citrate-capped AuNPs with S^{2-} and thiourea (TU) as inputs, and devised a colorimetric sensor for the logic sensing of S^{2-} in real samples.

Experimental

Chemical and apparatus

Sodium sulfide ($Na_2S·9H_2O$), ethylenediaminetetraacetate (EDTA) and chloroauric acid ($HAuCl_4·4H_2O$) were brought from Aladdin Reagent Company (Shanghai, China). Thiourea (TU) and trisodium citrate were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Other reagents and chemicals were at least analytical reagent grade. Double distilled water was used throughout experiments.

The UV-visible spectra of citrate-capped AuNPs were recorded by a Shimadzu UV-2450 spectrophotometer (Shimadzu, Japan).

Synthesis of the AuNPs

All glassware used in the following procedures was cleaned in a bath of freshly prepared solution of HNO_3-HCl (1:3, V/V), rinsed thoroughly in water and dried in air prior to use. AuNPs colloids with an average diameter of 13 nm were prepared according to previously published protocols.[25] Briefly, 1 mL of 1% $HAuCl_4$ solution

was dissolved in 100 mL of water and boiled. 3 mL of 1% trisodium citrate solution was quickly added to the refluxed $HAuCl_4$ solution, resulting in a color change from pale yellow to deep red, indicating the formation of gold nanoparticles. After a continuous reflux for an additional 15 min, the solution was slowly cooled down to room temperature. The wine-red solution of AuNPs was stored at 4 °C in refrigerator. The particle concentration of AuNPs (ca. 3.1 nM) was determined according to Beer's law using an extinction coefficient of ca. 2.7×10^8 M^{-1} cm^{-1} at 520 nm for 13 nm AuNPs.[26]

Sample pretreatment

For real samples analysis, various real samples including river water, mineral water, tap water, human urine, monosodium glutamate, sugar, and white wine, were tested. River water was collected from the Minjiang River, Fujian Province, China. Tap water was collected from our laboratory. Human urine was collected from a healthy man. Mineral water, monosodium glutamate, sugar, and white wine were collected from the local supermarket. Sample pretreatment process was as follows. For river water, mineral water, and tap water, the collected sample (10 mL) was filtered through a 0.22 μm membrane at first, and then 0.1 mM EDTA was added to the filtrate. Finally, the solution was adjusted to pH 9.0 with 2 M NaOH. For human urine and white wine, the collected sample (10 mL) was directly adjusted to pH 9.0 with 2 M NaOH. For monosodium glutamate and sugar, 0.1 g sample was dissolved in 10 mL water and then the solution was adjusted to pH 9.0 with 2 M NaOH.

Logic test for S^{2-}

Sample solutions with and without standard addition are referred to Spiked and Unspiked, respectively. For Spiked samples, known amounts of S^{2-} were added into samples. The samples were determined according to the following steps. 0.2 mL of the sample solution containing 5 μM TU was mixed with 0.2 mL AuNPs solution. The solution was incubated in a 30 ℃ water bath for 3 min. The output signals were monitored by naked eyes or UV-visible spectrophotometer.

Results and discussion

Construction of INHIBIT logic gate

The as-prepared AuNPs showed a distinctive wine-red color with the absorption peak at 520 nm. These AuNPs were relatively stable owing to the electrostatic repulsion invoked by citrate ligands adsorbed on the particles surface. With the addition of TU, the AuNPs rapidly aggregated, along with the consequent shift of the absorption peak to longer wavelength, i.e., 680 nm and a gradual color change from wine-red to blue (Fig. 1). Containing sulfur atom, TU molecule can absorb on the surface of AuNPs through Au-S bond and replace the original negative citrate ligand. With a pK_a of 2.0, TU remains in the neutral form from pH=2 to pH=10.[27] Therefore, the adsorption of TU on the surface of AuNPs results in significantly reduced overall surface charges and increased van der Waals attractive force among nanoparticles, promoting the aggregation of AuNPs. In our experiment, it was found that urea, which is structurally similar to TU, could not induce the aggregation of AuNPs, revealing that S atom rather than amino groups of TU plays a key role in the interaction between TU and AuNPs. Interestingly, the introduction of S^{2-} could prevent the aggregation of AuNPs induced by TU. It is due to the competitive combination of S^{2-}, which also has high affinity to AuNPs, with TU. Consequently, we expected this phenomenon to act as a INHIBIT logic gate,[28] the true output of which is generated when only one input is present without the other input. This logic gate is unique in that it demonstrates noncommutative behavior, i.e. one input has the power to disable the whole system, thus being different from the previous commutative OR, AND, and XOR gates.[29] For proof-of-concept, we established a logic gate upon the addition of S^{2-} and TU as the two inputs, and color change of AuNPs as outputs. For input, we defined the presence of S^{2-} or TU as "1", and the absence as "0". For output, the well-dispersed red AuNPs solution is defined as "0" and the blue solution with AuNPs aggregates as "1". Scheme 1 illustrates the working principle of the colorimetric logic gate. With no input or with S^{2-} input alone, citrate-capped AuNPs well dispersed with an output of "0". With TU input alone, citrate-capped AuNPs aggregated and color of the solution changed from wine-red to blue, giving an output signal of "1". When the system was subjected to the two inputs together, the introduction of S^{2-} prevented the

aggregation of AuNPs induced by TU, and the color output signal was "0". Therefore, only the addition of TU would generate a positive output signal "1", which is in accord with the proper execution of the INHIBIT logic gate.

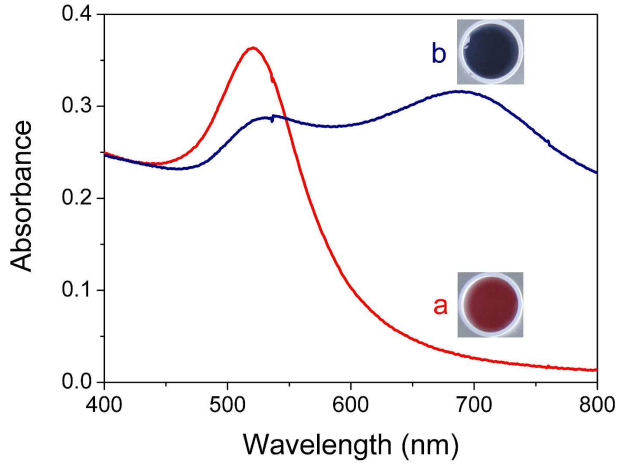
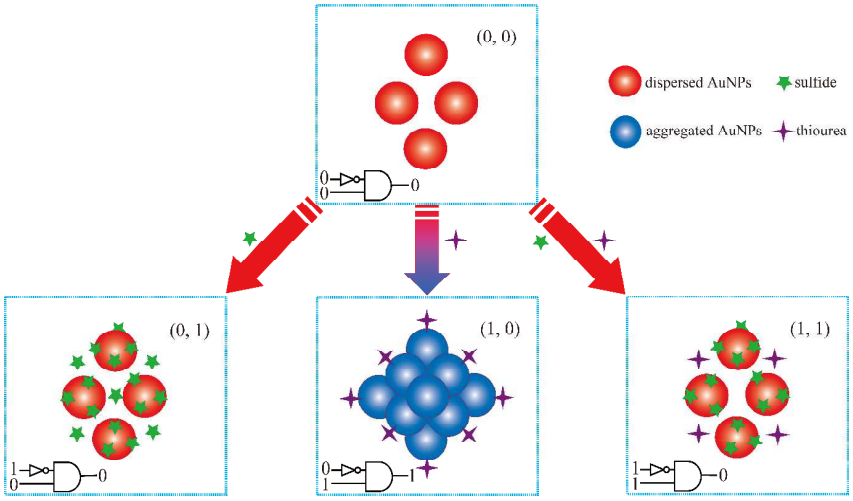


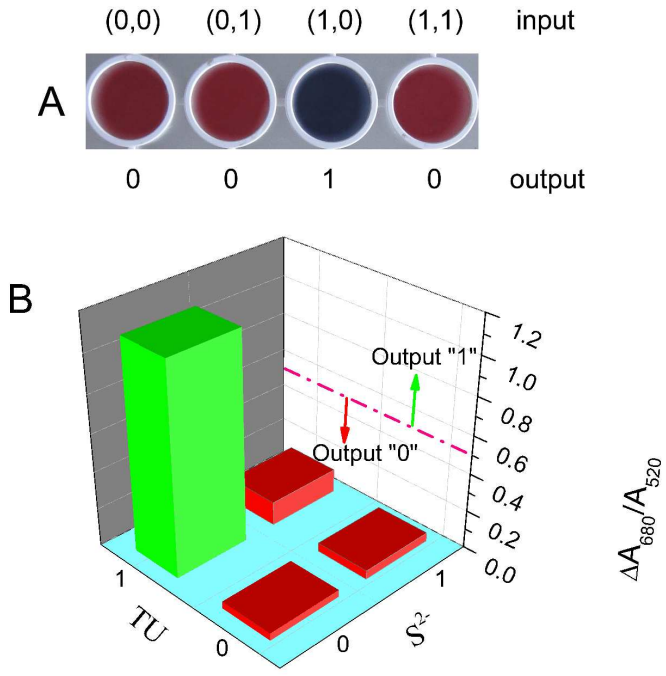
Fig. 1 The absorption spectra of (a) citrate-capped AuNPs+9 μM S^{2-}+5 μM TU and (b) citrate-capped AuNPs+5 μM TU. Inset: the corresponding photographs. Conditions: pH: 9, and incubation time: 3 min.



Scheme 1 Schematic illustration of the AuNPs based colorimetric logic gate.

Fig. 2A shows the color response of the INHIBIT logic system upon treatment with S^{2-} and TU inputs. In the presence of TU input (1, 0), the color of the solution turned

to blue; while in the absence of both inputs (0, 0), in the presence of S^{2-} input (0, 1), or both the two inputs (1, 1), the color of the solution remained red. The values of absorption ratio (A_{680}/A_{520}) toward different inputs were further calculated, with the output ratio below and above the threshold value of 0.5 defined as "0" and "1", respectively. It can be seen that only the presence of TU input obtained an output 1, while the other cases obtained output 0 (Fig. 2B). A truth table is given in Fig. 2C.



Inputs		Outputs	
TU (5 μM)	S^{2-} (9 μM)	Color of AuNPs	A_{680}/A_{520}
0	0	0 (red)	0 (low)
0	1	0 (red)	0 (low)
1	0	1 (blue)	1 (high)
1	1	0 (red)	0 (low)

C

Fig. 2 Operation of the INHIBIT logic. (A) Visual color outputs. (B) Bar-chart presentation of the absorbance outputs. (C) Truth table corresponding to the INHIBIT

logic gate. Conditions: pH: 9, and incubation time: 3 min.

TU-AuNPs system for logic sensing of S^{2-}

As described above, the logic behavior of the proposed system is INHIBIT, the true output of which is generated when only one input is present without the other input, wherein the red-to-blue color change happens when TU is the only input. According to the experimental results, the introduction of S^{2-} could prevent the aggregation of AuNPs induced by TU, suggesting that TU-AuNPs systems might be a good probe for S^{2-} detection. Next, the TU-AuNPs system for logic sensing of S^{2-} was carefully studied.

Optimization of assay conditions

Media pH influences the stability of citrate-capped AuNPs due to the protonation/deprotonation of the ligand. Since TU is a weak base with a pK_a of 2.0 and sulfide exists in three species (H_2S, HS^-, and S^{2-}) in solutions defined by its pK_a, media pH also affects the form of TU and sulfide in aqueous solution. So media pH plays an important role in the interaction among AuNPs, TU and sulfide. We investigated the effect of pH in the range from 5 to 10 and the results are show in Fig. S1. The absorbance of the solution at 680 and 520 nm corresponded to the quantities of aggregated and dispersive AuNPs, respectively. Thus, the molar ratio of aggregated AuNPs to dispersive ones can be expressed by the ratio of the absorbance at 680 nm to that at 520 nm (A_{680}/A_{520}). With the addition of TU that remains in neutral form under the experimental conditions, AuNPs aggregated due to the replacement of the surface bounded negative citrate ligands by neutral TU. This particle aggregation was, however, suppressed by S^{2-}, which also has high affinity to AuNPs. It can be seen that the highest increment of the absorbance ratio ($\Delta A_{680}/A_{520}$) was obtained at pH 9. This phenomenon can be explained by the fact that more charged, less protonated species (i.e. HS^-, S^{2-}) formed at higher pH status, which compete with neutral TU molecule for combination with AuNPs resulting in the well-dispersed AuNPs. Hence, all subsequent experiments were carried out with a media pH of 9.

Since TU was used as the aggregation promoter of AuNPs, its concentration

directly had an influence on the response of S^{2-} ($\Delta A_{680}/A_{520}$ value). When the concentration of TU was too low, it can not lead to complete aggregation of AuNPs. On the contrary, when the concentration of TU was too high, the sensitivity for S^{2-} determination decreased. The effect of the concentration of TU from 0 to 7 μM was tested. The results showed that the maximum $\Delta A_{680}/A_{520}$ value was readily observed when the concentration of TU was 5 μM (Fig. S2). To obtain high sensitivity, the concentration of TU was selected as 5 μM in the subsequent tests.

The kinetics of S^{2-} preventing aggregation of AuNPs induced by TU was investigated. It can be seen from Fig. S3 that the absorbance ratio (A_{680}/A_{520}) first leaped with an increase of the incubation time (0-3 min) and then varied slightly. Hence, all subsequent experiments were carried out with an incubation time of 3 min.

Sensitivity

Under the optimum conditions mentioned above, we evaluated the sensitivity of this new sensor towards S^{2-}. Upon addition of increasing concentrations of S^{2-}, the anti-aggregation ability of S^{2-} for citrate-capped AuNPs became increasingly powerful, along with the absorption peak at 680 nm increased while that at 520 nm decreased (Fig. 3A) and a gradual color change from blue to wine-red (Fig. 3A, inset). It should be noted that 4 μM S^{2-} would induce a distinct color change, which indicated that this low concentration of S^{2-} could be detected by naked eyes. The absorbance ratio (A_{680}/A_{520}) gradually decreased with the addition of increasing concentrations of S^{2-} (Fig. 3B). The calibration curve for the absorbance ratio against S^{2-} concentration was linear in the range from 2 to 9 μM (Fig. 3B, inset) and fit the linear equation A_{680}/A_{520}=-0.1336C (μM) + 1.3446 (r=0.997). The relative standard deviation was 1.3% for the determination of 4 μM S^{2-} (n=6).

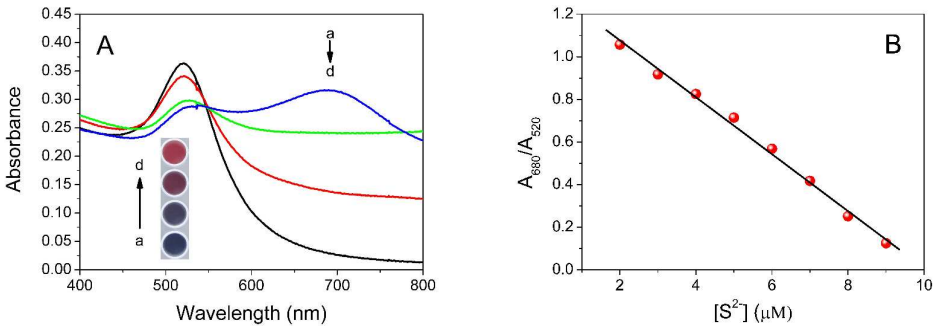


Fig. 3 (A) The absorption spectra of sensing systems in absence and presence of different amounts of S^{2-}. The concentrations of S^{2-} are (a) 0 μM, (b) 4 μM, (c) 7 μM, and (d) 9 μM, respectively. Inset: the corresponding photographs. (B) Effect of S^{2-} on the absorbance ratio (A_{680}/A_{520}) of sensing system. Inset: The linear relationship between A_{680}/A_{520} and the concentration of S^{2-}. Conditions: pH: 9, TU concentration: 5 μM, and incubation time: 3 min.

Selectivity

Selectivity is a very important parameter to estimate the performance of a sensor. The selectivity of our constructed system involves two sides. On the one hand, to check for false positive signals, various molecules, such as ascorbic acid (AA), lactose (Lac), glucose (Glu), urea, cysteine (Cys), ethanol (Eth), bovine serum albumin (BSA) and glutathione (GSH), were investigated to evaluate the selective response of TU towards AuNPs. Fig. 4A shows visual color change and absorbance ratio of the AuNPs in the presence of TU and other interferences. It is clearly observed that only TU induced a dramatic color change from wine-red to blue but the others with concentration of 20 times higher than that of TU could not induce the aggregation of AuNPs. These results proved the distinct capability of our constructed system to avoid producing false positive signals. On the other hand, to check for false negative signals, we investigated the response of TU-AuNPs system in the presence of various ions. As manifested in Fig. 4B and Fig. 4C, none of anions except for S^{2-} could prevent the TU induced aggregation of AuNPs and most cations showed no interference for this

method. It's worth noting that under the conditions employed here, polysulfide fail to appear because sulfur is not being produced by oxygenation of sulfide when pH values are greater than 9.[30] Thus, the interference from polysulfide can be avoided. Cu^{2+}, Mn^{2+}, Al^{3+} and Fe^{3+} could interfere the assay at high concentration. However, with the help of EDTA, which is a strong metal ion chelator, the interferences from these cations with concentration of 10 times higher than that of S^{2-} can be ignored. These results demonstrated the excellent selectivity of this approach applied in S^{2-} detection.

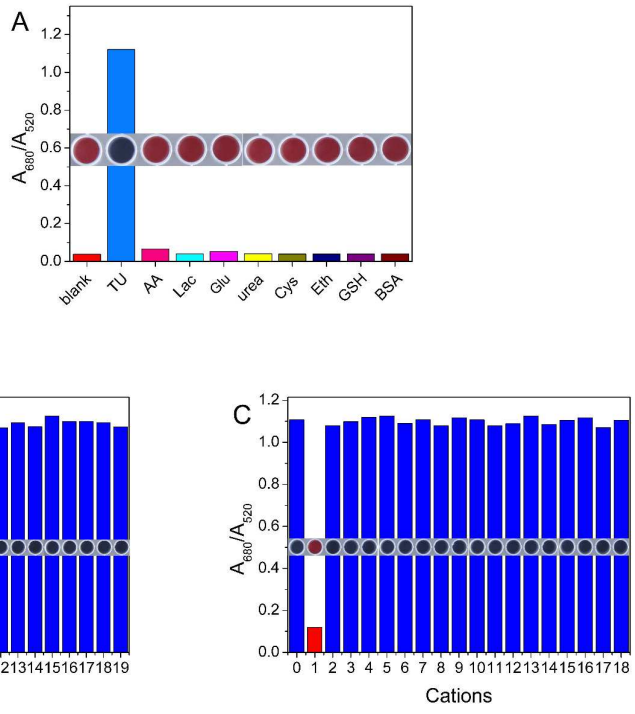
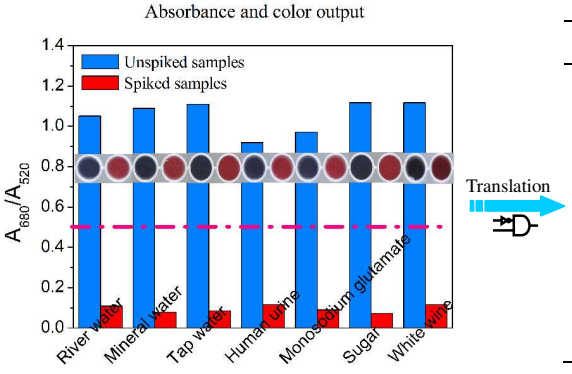


Fig. 4 (A) The colorimetric response of the sensing system in the absence and presence of AA, Lac, Glu, urea, Cys, Eth, BSA and GSH (100 μM each), as well as TU (5 μM). (B) The colorimetric response of the sensing system in the absence and presence of various anions. Samples marked with 0-19 corresponding to blank, S^{2-}, $S_2O_3^{2-}$, I^-, SCN^-, $S_2O_8^{2-}$, SO_4^{2-}, SO_3^{2-}, Cl^-, F^-, Br^-, BrO_3^-, IO_3^-, ClO_4^-, Ac^-, NO_3^-, NO_2^-, HPO_4^{2-}, CO_3^{2-} and $EDTA^{2-}$, respectively. (TU: 5 μM; S^{2-}: 9 μM; $S_2O_3^{2-}$: 9 μM, I^-: 45 μM, other anions: 90 μM each); (C) The colorimetric response of the sensing system in the absence and presence of various cations. Samples marked with 0-18

corresponding to blank, S^{2-}, Cu^{2+}, Mn^{2+}, Al^{3+}, Fe^{3+}, K^{+}, Na^{+}, Ca^{2+}, Mg^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Ba^{2+}, Cd^{2+}, Pb^{2+}, NH_4^{+} ,and Cr^{3+}, respectively. (TU: 5 μM; S^{2-}: 9 μM; Al^{3+}: 9 μM; Fe^{3+}: 9 μM; Cu^{2+}: 45 μM; Mn^{2+}: 45 μM; other cations: 90 μM each) Conditions: pH: 9, and incubation time: 3 min.

Logic sensing S^{2-} in real samples

Since most of the ions and molecules did not interfere, we believe that this logic gate will operate finely in the S^{2-} assay for relatively complex matrix systems. In order to illustrate this proposal, several real samples, including river water, mineral water, tap water, human urine, monosodium glutamate, sugar, and white wine, were employed as potential practical subjects containing S^{2-}. For all samples, both unspiked and spiked, the states of TU were "1". According to the results of the logic gate operation showed in Fig. 5, the states of output were "1" for all unspiked samples, indicating that no S^{2-} was detected (in the "0" state), while the states transformed to "0" for all samples after the standard spiking (in the "1" state), showing usefulness of the INHIBIT gate in the logic detection of S^{2-} in various practical samples.



Logic input & Logic output results

Samples	Unspiked	Spiked
River water	0&1	1&0
Mineral water	0&1	1&0
Tap water	0&1	1&0
Human urine	0&1	1&0
Monosodium glutamate	0&1	1&0
Sugar	0&1	1&0
White wine	0&1	1&0

Fig. 5 Application of the established INHIBIT logic gate for S^{2-} sensing in various real samples. The logic gate translates absorbance (left) and visual color (inset, left) outputs of unspiked and spiked samples to logical outputs and thence to logical input results, i.e. the presence of S^{2-} (right). For spiked samples, the concentrations of S^{2-} were all 10 μM. Conditions: pH: 9, TU concentration: 5 μM, and reaction time: 3 min.

Conclusion

In summary, we designed a noncommutative logic gate (INHIBIT gate) by utilizing citrate-capped AuNPs as a signal transducer with sulfide and TU as mechanical activators. Based on the logic gate, a colorimetric sensor was devised for inexpensive, label-free, rapid, sensitive and selective determination of S^{2-}. The distinctive advantage of this system is that recognition events can be translated into a color change of the solution, which can be monitored by UV-visible spectroscopy or even the naked eyes. Moreover, this logic gate was successfully applied for S^{2-} sensing in various practical samples, implying its extensive applications in food, environment, and biological system.

Acknowledgement

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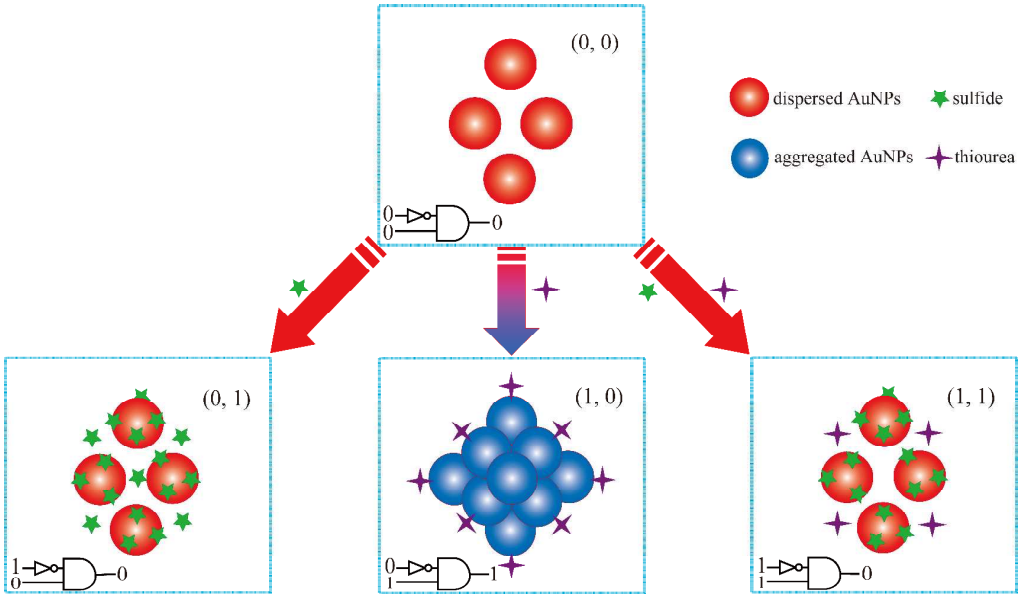
344 **TOC**



345

346 An INHIBIT logic gate is designed based on citrate-capped gold nanoparticles and

347 successfully utilized to the determination of sulfide.