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ARTICLE

Glutathione-facilitated design and fabrication of gold nanoparticles-based logic gates and keypad lock

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Zhenzhen Huang, Haonan Wang, Wensheng Yang*

In this paper, we developed a simple design and fabrication of logic gates and device by using a commercially available tripeptide, glutathione (GSH) together with metal ions and EDTA to control the dispersion and aggregation of gold nanoparticles (NPs). With the fast adsorption of GSH on gold NPs and the strong coordination of GSH with metal ions, the addition of GSH and Pb^{2+} ions immediately resulted in the aggregation of gold NPs, giving rise to an AND function. Either Pb^{2+} or Ba^{2+} ions induced the aggregation of gold NPs in the presence of GSH, supporting an OR gate. Based on the fact that EDTA (disodium ethylenediaminetetraacetate) has a strong capacity to bind metal ions, thus preventing the aggregation of gold NPs, an INHIBIT gate was also fabricated. More interestingly, we found that the addition sequence of GSH and Hg^{2+} ions influenced on the aggregation of gold NPs in a controlled manner, which was used to design a sequential logic gate and a three-input keypad lock for potential use in information security. The GSH strategy addressed concerns of low cost, simple fabrication, versatile design and easy operation, and offered a promising platform for development of functional logic systems.

Introduction

Colloidal gold nanoparticles (NPs) have been attracting extensive attentions due to their excellent chemical stability and characteristic plasmon absorption in visible region which can be easily observed by naked eyes.¹⁻² An interesting feature is that such gold NPs in red color become purple or blue upon aggregation. Recent works demonstrated the attractive feasibility to simulate electronic logic gates, the key components in information processing and storage, using specific stimuli as inputs to control over the dispersion/aggregation of the gold NPs and the resulting color change as outputs.³⁻⁵ For example, by employing typical citrate-capped gold NPs, Chen *et al.* fabricated an INHIBIT logic gate based on the event that the Hg^{2+} ions could prevent the aggregation of gold NPs induced by melamine.⁶ In order to construct more logic gates, generally it is necessary to modify gold NPs with carefully-designed DNA oligomers and organic

ligands. Taking advantage of the DNA-modified gold NPs, a series of logic gates (AND, OR and INHIBIT, *etc.*) were developed by Zhang *et al.* by using ion-dependent DNAs (DNA with catalytic activity) as functional components and the metal ions as inputs.⁷ Jiang *et al.* developed AND, OR and INHIBIT gates by using gold NPs modified with predesigned spiropyran-containing alkanethiols which were sensitive to both UV light and Cu^{2+} ions.⁸ These logic gates have been considered to have great potentials in biosensing, molecular computation and information security. However, the design and synthesis of DNA and functional organic molecules are time-consuming and often require the use of toxic solvents. Therefore, it is highly desirable to fabricate gold NPs-based logic gates in a more economical and simple manner.

Glutathione (γ -Glu-Cys-Gly, GSH) is a commercially available tripeptide containing multiple functional groups such as thiol, amine and carboxylic acid. It is known that the thiol

group of GSH has high binding affinity to the surface of gold NPs, and the amine and carboxylic acid groups of GSH can interact with a variety of metal ions.⁹⁻¹² Here, several logic gates were developed by using the GSH-facilitated dispersion and aggregation of gold NPs. Based on the fast adsorption of GSH on the surface of gold NPs and the strong coordination of GSH with metal ions, the addition of GSH and Pb^{2+} ion immediately resulted in the aggregation of gold NPs, giving rise to an AND function. Moreover, either Pb^{2+} or Ba^{2+} ions induced the aggregation of gold NPs in the presence of GSH, supporting an OR gate. In addition, based on the fact that EDTA (disodium ethylenediaminetetraacetate) has a strong capacity to bind metal ions, thus preventing the aggregation of gold NPs, an INHIBIT gate was fabricated. More interestingly, it was found that the sequence for the addition of GSH and Hg^{2+} ions had a significant impact on the aggregation behavior of gold NPs, which can be used to design a sequential logic gate and a keypad lock that was of great significance for information security.

Experimental Section

Materials and Measurements

Hydrogen tetrachloroaurate (III) ($\geq 99.9\%$), sodium citrate tribasic dehydrate ($\geq 99.0\%$) and EDTA were purchased from Sigma-Aldrich and used without further purification. Glutathione was purchased from Sangon (Shanghai, China). Other reagents were all of analytical reagent grade and used as received. UV-Vis absorption spectra were acquired by using a Shimadzu UV-1800 spectrophotometer. Transmission electron microscopy (TEM) observations were conducted on a JEOL 1200 electron microscope operating at an accelerating voltage of 100 kV using carbon-coated copper grids as substrates. Dynamic light scattering (DLS) measurements were performed on Brookhaven BI-90 Plus particle size analyzer with a scattering angle of 90° .

Preparation of gold NPs

Gold NPs were prepared through a modified Frens method.¹³ An aqueous solution of HAuCl_4 (0.25 mM, 50 ml) was heated under reflux and then 1.3 mL solution of sodium citrate (1%) was added under vigorous stirring. The solution was kept on boiling for 15 min. The concentration of the gold NPs of ~15 nm in size was calculated to be 2.4 nM by assuming that the complete reduction from Au^{3+} to Au^0 atoms.

Quantitative GSH binding measurement

GSH (0.4 mM) was added to an aqueous solution of gold NPs (2 nM), incubating for 5 min, 6 h and 8 h, respectively. The samples were then centrifuged at 12000 rpm for 20 min. The amount of free GSH remained in the supernatant was quantified by using Enzychrom™ GSH/GSSH Assay Kit (EGTT-100, Biosassay System, USA). GSH tethered on the surface of gold NPs was calculated from the difference between the amount of GSH added initially minus the amount free GSH in supernatant. The surface coverage was calculated from the measured amount

of adsorbed GSH on each gold NP, the cross section of a GSH (0.494 nm^2) and the surface area of gold NP (706.5 nm^2 for 15 nm gold NPs).¹⁴

AND logic gate

An aqueous solution of gold NPs (2 nM) was added into a tube. The AND operation was triggered by the addition of the four possible combinations of inputs: 1) H_2O (0, 0); 2) 0.4 mM GSH (1, 0); 3) 0.1 mM Pb^{2+} ions (0, 1); 4) 0.4 mM GSH + 0.1 mM Pb^{2+} ions (1, 1). The effect of NaCl and pH on the logic performance was carried out by the addition of certain amounts of NaCl, NaOH or HCl to gold NPs solution.

OR logic gate

The amount of GSH (0.4 mM) was firstly added to an aqueous solution of gold NPs (2 nM). The OR operation was triggered by the addition of the four possible combination of inputs: 1) H_2O (0, 0); 2) 0.15 mM Ba^{2+} ions (1, 0); 3) 0.15 mM Pb^{2+} ions (0, 1); 4) 0.15 mM Ba^{2+} ions + 0.15 mM Pb^{2+} ions (1, 1).

INHIBIT logic gate

The amount of GSH (0.4 mM) was firstly added to the aqueous solution of gold NPs (2 nM). The INHIBIT operation was triggered by the addition of the four possible combinations of inputs: 1) H_2O (0, 0); 2) 0.1 mM Pb^{2+} ions (1, 0); 3) 1 mM EDTA (0, 1); 4) 0.1 mM Pb^{2+} ions + 1 mM EDTA (1, 1).

Sequential logic gate

An aqueous solution of gold NPs (2 nM) was added into a tube. The sequential gate was performed by the addition of inputs (GSH and Hg^{2+} ions) in different combinations and order. 1) H_2O ; 2) 0.4 mM GSH; 3) 0.3 mM Hg^{2+} ions; 4) 0.4 mM GSH was added, incubating for 15 min, then 0.3 mM Hg^{2+} ions was added; 5) 0.3 mM Hg^{2+} ions was added and incubated for 15 min, then 0.4 mM GSH was added.

Keypad lock

An aqueous solution of gold NPs (2 nM) was used as an initial state. The keypad lock was operated by the addition of the three inputs (0.4 mM GSH, 0.3 mM Hg^{2+} ions and 1 mM EDTA) in different order. 1) Hg^{2+} ions – GSH – EDTA (HGE); 2) Hg^{2+} ions – EDTA – GSH (HEG); 3) EDTA – GSH – Hg^{2+} ions (EGH); 4) EDTA – Hg^{2+} ions – GSH (EHG); 5) GSH – EDTA – Hg^{2+} ions (GEH); 6) GSH – Hg^{2+} ions – EDTA (GHE). The interval of adding each input was 15 min.

Results and discussion

AND logic gate

It is reported that GSH can tether on the surface of gold NPs through the formation of Au-S bond.^{12,15} Figure 1A showed that when GSH was added into the solution of gold NPs, the UV-Vis absorption spectra shifted slightly from 518 to 520 nm, associated with the attachment of GSH on gold NPs.¹⁶ The addition of Pb^{2+} ions alone had no significant impact on the absorption spectra. However, when GSH and Pb^{2+} ions were

added simultaneously, the spectra of gold NPs dramatically red-shifted to 525 nm and showed a new absorbance peak around 630 nm with the color change from red to blue. This can be attributed to the aggregation of gold NPs induced by the coordination interaction of Pb^{2+} ions with GSH tethered on gold NPs.^{11-12,17} The gold NPs aggregation was further confirmed by TEM analysis (Supporting Information Figure S1). Intrigued by that, a gold NPs-based colorimetric AND logic gate was designed (Figure 1B). The AND gate is represented by the situation in which the output value is "1" only when both input values are "1", while in all other cases the output value is "0". To perform an AND operation, GSH and Pb^{2+} were employed as inputs. The absence and presence of each input was defined as "0" and "1", respectively. Meanwhile, the color change of solution was used as an output signal. The red solution containing dispersed gold NPs was defined as "0" and the blue solution containing aggregated gold NPs was defined as "1". In the absence of both inputs, gold NPs were well-dispersed in solution, exhibiting a red color (output = 0). Similarly, no significant color change was observed in the presence of either input. Only the presence of both inputs resulted in a color change from red to blue (output = 1), supporting an AND logic gate. The AND logic operation was further confirmed by monitoring the UV/Vis absorption spectra. The absorbance at 520 and 620 nm are related to the quantities of the dispersed and aggregated gold NPs respectively. Thus, the absorbance ratio of gold NPs at these two wavelengths A_{620}/A_{520} is generally used to indicate the aggregation state of gold NPs. As shown in Figure 1D, a higher value of A_{620}/A_{520} (>0.5) was obtained only in the presence of both inputs.

Response time of the AND gate

Figure 2A illustrated that the value of A_{620}/A_{520} of gold NPs solution increased immediately following the addition of inputs (GSH and Pb^{2+} ions) and reached a plateau in less than 10 min. The quick response was partially attributed to the fast adsorption of GSH on the surface of gold NPs. DLS study revealed that the hydrodynamic diameter of gold NPs increased from 21.4 ± 0.1 to 22.8 ± 0.1 after mixing with GSH for 5 min (Supporting Information Figure S2). The 1.4 nm increase of the hydrodynamic diameter was consistent with previous report of the size of GSH, indicating the adsorption of GSH.¹⁴ Further aging had little influence on the hydrodynamic diameter of gold NP, suggesting that GSH adsorbed onto gold NP within the first 5 min under our experimental conditions. Moreover, the quantitative binding measurements showed that the surface coverage of GSH on gold NPs only increased from about 42% in the 5 min sample to about 45% in the 6 h sample. Further prolonged incubation time had no significant impact on the amount of tethered GSH (8 h, ~45%). This result was consistent with the recent adsorption kinetics study of thiol compounds onto gold NPs.¹⁸⁻¹⁹ The fast adsorption of GSH on the surface of gold NPs enabled GSH to act as both a functional ligand for NPs modification and an input to trigger the logic operation.

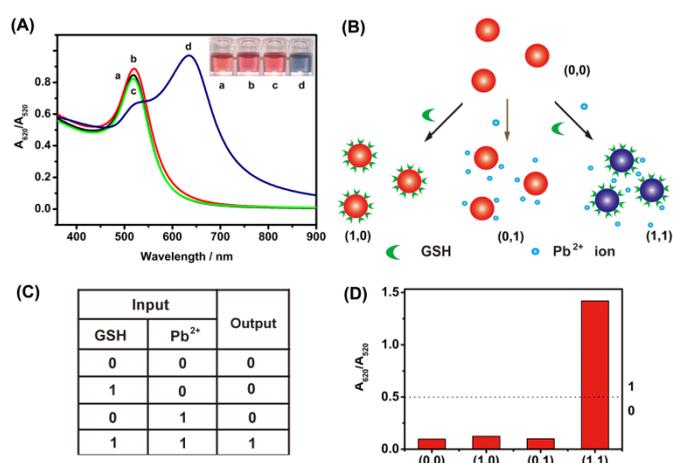


Figure 1. AND logic gate design and fabrication. A) UV-Vis absorption spectra and optical photographs (inset) of a) gold NPs alone, b) gold NPs + GSH, c) gold NPs + Pb^{2+} ions and d) gold NPs + GSH + Pb^{2+} ions. B) Scheme of AND logic gate in the presence of no input (0, 0), GSH alone (1, 0), Pb^{2+} ions alone (0, 1) and both GSH and Pb^{2+} (1, 1). C) Truth table and D) Values of absorbance ratio (A_{620}/A_{520}) of AND gate.

Influence of NaCl on the AND gate

The effect of NaCl on the logic performance was investigated. As shown in Figure 2B, the AND gate was active at a range of NaCl concentration from 0–30 mM. Further increasing the concentration of NaCl could lead to the aggregation of gold NPs even in the absence of inputs because NaCl is able to reduce the electrostatic repulsion among the neighboring gold NPs, thus accelerating the aggregation.²⁰ In addition, it was revealed that the response time of the AND gate was greatly reduced as the increasing concentration of NaCl (Supporting Information Figure S3). For example, in the presence of 10 mM NaCl, the value of A_{620}/A_{520} reached a plateau in less than 1 min. The fast response was very important for the practical application of logic gate.

Influence of pH on the AND gate

Solution pH is another important parameter for the logic performance. As shown in Figure 2C, when solution pH was below 5.0, the presence of GSH alone significantly increased the value of A_{620}/A_{520} , which might be due to the interparticle assembly of GSH-modified gold NPs through hydrogen-bonding.²¹ The AND gate worked well at the pH range of 5.0 to 8.0. It is reported that Pb^{2+} ions can bind to the thiol and carboxylate group of GSH.⁹ In the presence of gold NPs, the thiol group is linked to gold NP. Thus, Pb^{2+} ions mainly bind with the carboxylate group.¹¹ At pH 5–8, the carboxylic acid group (pKa 3.22) was completely deprotonated, thus significantly promoted the Pb^{2+} ions-induced gold NPs aggregation. However, when solution pH increase above 8.0, hydroxyl groups could compete with carboxylate group to bind Pb^{2+} ions, thus inhibiting the aggregation of gold NPs.¹²

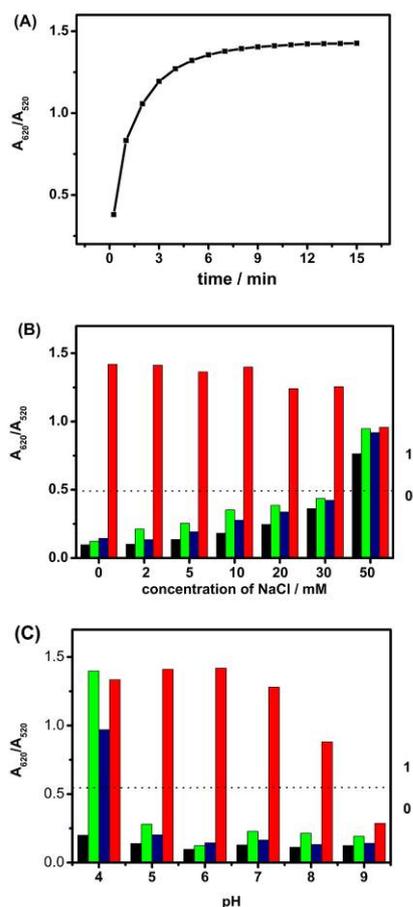


Figure 2. A) Time-dependent values of absorption ratio (A_{620}/A_{520}) upon the addition of both GSH and Pb^{2+} ions. The influence of B) the concentration of NaCl and C) pH on the AND performance. Values of absorption ratio (A_{620}/A_{520}) of AND gate in the presence of no input (black), GSH alone (green), Pb^{2+} ions alone (blue) and both GSH and Pb^{2+} ions (red).

OR logic gate

The response of gold NPs to other metal ions in the presence of GSH was also studied (Figure 3). At the concentration of 0.10 mM, the addition of metal ions including Li^+ , Na^+ , K^+ , Cs^+ , Ca^{2+} , Mg^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Hg^{2+} , Fe^{2+} , Fe^{3+} , Ba^{2+} , Co^{2+} , Mn^{2+} and Al^{3+} had little influence on the value of A_{620}/A_{520} . Only 0.10 mM of Pb^{2+} ions could lead to the aggregation of gold NPs. This was quite consistent with previous investigation on the specific response of GSH-coated gold NPs and nanorods to Pb^{2+} ions, which is mainly due to the high affinity of Pb^{2+} ions to GSH tethered on the particle surface.^{11,17,22} At higher concentration (0.15 mM) of metal ions, it was identified that Ba^{2+} could also cause the aggregation of gold NPs as Pb^{2+} ions did. By further increasing the concentration to 0.30 mM, various ions such as Ca^{2+} , Mg^{2+} , Ni^{2+} , Hg^{2+} , Ba^{2+} , Mn^{2+} and Al^{3+} could result in the aggregation of the NPs. This concentration-dependent selectivity of gold NPs toward metal ions in the presence of GSH could be used to fabricate an OR logic gate by using Pb^{2+} and Ba^{2+} ions as inputs (Figure 4). The OR gate is represented by the situation in which the output value is 1 if either input values are 1. Similar to AND gate, the

absence and presence of metal ions input was defined as ‘‘0’’ and ‘‘1’’, respectively. The red-to-blue color change occurred in the presence of either or both inputs, which was consistent with the OR logic function. The OR operation was also confirmed by absorption spectra. Figure 4D illustrated that a high value of A_{620}/A_{520} was obtained in the presence of either or both inputs while much lower value of A_{620}/A_{520} was acquired in the absence of inputs. It was noted that the logic behavior of such OR gate would be interfered under high concentration of metal ions (≥ 0.30 mM). Using polypeptides with higher specificity to metal ions and better protection against salt would be helpful to improve the stability and performance of the logic gate.

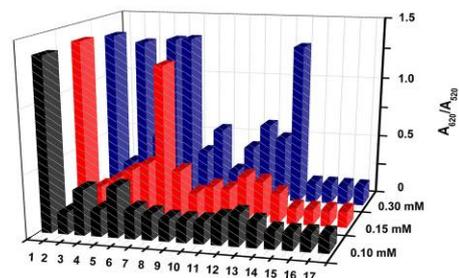


Figure 3. The response of gold NPs to different concentrations of metal ions in the presence of GSH. 1) Pb^{2+} , 2) Fe^{2+} , 3) Mn^{2+} , 4) Co^{2+} , 5) Al^{3+} , 6) Ba^{2+} , 7) Fe^{3+} , 8) Hg^{2+} , 9) Zn^{2+} , 10) Cu^{2+} , 11) Ni^{2+} , 12) Mg^{2+} , 13) Ca^{2+} , 14) Cs^+ , 15) K^+ , 16) Na^+ and 17) Li^+ ions.

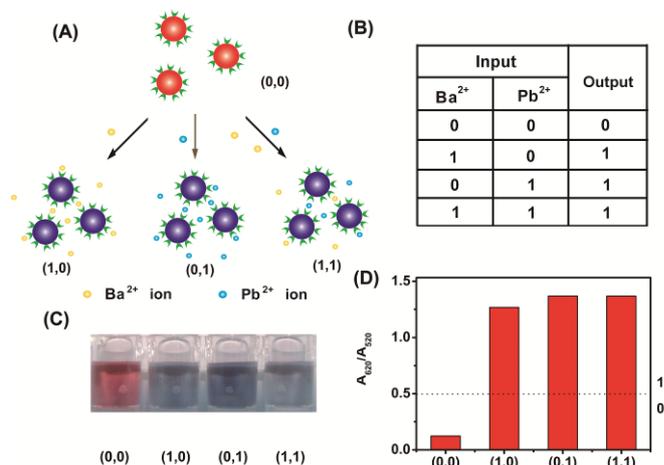


Figure 4. OR logic gate fabrication. A) Scheme of the OR gate in the presence of no input (0, 0), Ba^{2+} ions alone (1, 0), Pb^{2+} ions alone (0, 1), and both Ba^{2+} and Pb^{2+} ions (1, 1). B) Truth table C) Optical photographs and D) Values of absorption ratio (A_{620}/A_{520}) of the OR gate.

INHIBIT logic gate

By taking advantage the strong interaction of metal ions with chelating agent EDTA, an INHIBIT gate was constructed by using EDTA and Pb^{2+} ions as input. As shown in Figure 5, while EDTA alone had little influence on the color of GSH-gold NPs solution, simultaneous addition of EDTA and Pb^{2+} ions significantly inhibited the Pb^{2+} ions-induced aggregation of gold NPs because EDTA has strong chelating capacity for metal ions such as Pb^{2+} , Hg^{2+} , thus competing with GSH to

bind Pb^{2+} ions and supporting the INHIBIT function.^{8,22} The INHIBIT logic gate was also demonstrated by UV-Vis absorption spectra. A higher A_{620}/A_{520} was obtained with Pb^{2+} ions alone than those with other combinations of the inputs (Figure 5D).

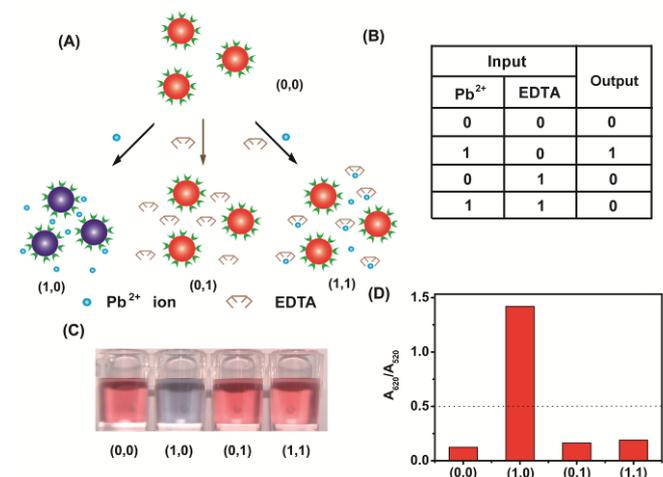


Figure 5. INHIBIT gate fabrication. A) Scheme of the INHIBIT gate in the presence of no input (0, 0), Pb^{2+} ions alone (1, 0), EDTA alone (0, 1) and both Pb^{2+} ions and EDTA (1, 1). B) Truth table C) Optical photographs and D) Values of absorption ratio (A_{620}/A_{520}) of the INHIBIT gate.

Sequential logic gate and keypad lock

The influence of the addition order of input on the logic performance was further studied. It was shown that simultaneous or sequential addition of GSH and Pb^{2+} ions had little impact on the aggregation of gold NPs (Supporting Information Figure S4). Similar results were obtained for Al^{3+} , Ca^{2+} , Ba^{2+} , Co^{2+} and Mn^{2+} ions. However, the adding sequence of GSH and Hg^{2+} ions dramatically influenced the aggregation behavior of gold NPs. When Hg^{2+} ions was added first to gold NPs solution and then GSH was added, a lower value of A_{620}/A_{520} was obtained than that acquired by simultaneous addition or addition of GSH followed by Hg^{2+} ions. The sequence-dependent output might be attributed to the high affinity metalphilic Hg-Au interaction. Recent researches suggest that aurophilic interaction including charge-induced dipole and dispersion interactions could induce the deposition of Hg^{2+} ions on gold NPs, which might hinder the coordination interaction between Hg^{2+} ions and tethered GSH, resulting the lower value of A_{620}/A_{520} .²³⁻²⁵ Based on this interesting phenomenon, a sequential logic gate could be thus constructed. Sequential gate is an important logic component in information processing, which is distinguished from simple logic gate as its outputs are not only dependent on the combination of inputs but also on the adding sequence of inputs.²⁶⁻²⁷ As shown in Figure 6, for the first input order, the addition of GSH followed by Hg^{2+} ions resulted in the color change from red to blue. When the input order was reversed, that is, the first input was Hg^{2+} ions followed by GSH, the solution remained red, demonstrating the sequential logic gate.

Previous works indicated that the combination of simple logic gates might offer the possibility to developed complex logic systems. For example, Ding *et al* designed a DNA-based logic device with programmed XOR and AND functions.²⁸ Chen *et al* developed a multi-addressable nanodevice to achieve Boolean computing by combining the molecular transport junctions-based AND and OR gates.²⁹ Here, by taking advantage of the sequential and INHIBIT gates described above, a keypad lock was further fabricated. Keypad lock is a logic device which is capable of processing password entries to restrict the number of persons that can access an object or data, thus plays a vital role in information security. The working principle of keypad lock is based on the fact that the output signal is determined by the appropriate combination of inputs in

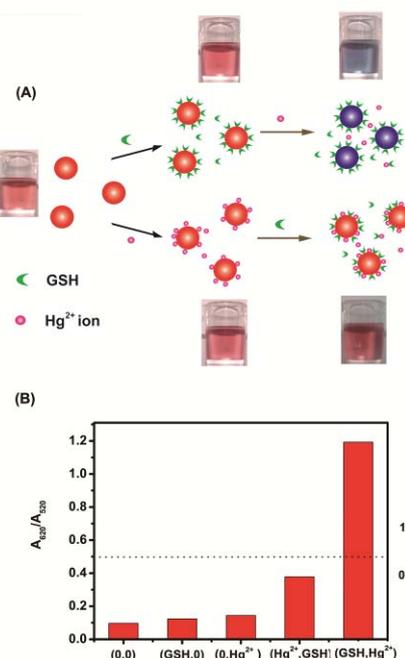


Figure 6. Fabrication of sequential logic gate. A) Scheme and optical photographs B) Values of absorption ratio (A_{620}/A_{520}) of the sequential gate.

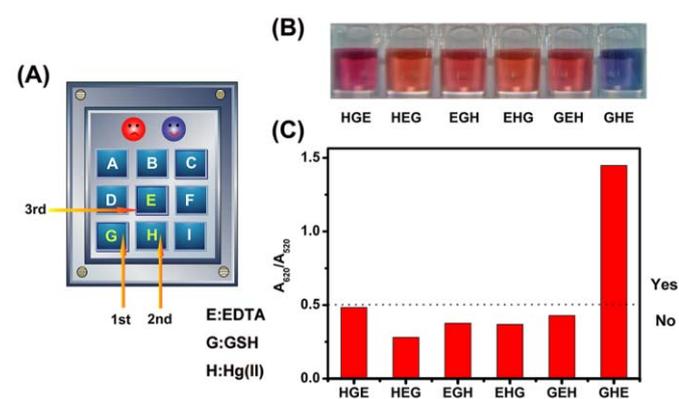


Figure 7. Fabrication of gold NPs-based keypad lock. A) Scheme B) Optical photographs and C) Values of absorption ratio (A_{620}/A_{520}) of the keypad lock.

a correct order. Traditional keypad lock is a mechanical or electronic device. During the past decade, much attention has been paid for simulating the function of keypad lock by using molecules and nanomaterials.³⁰⁻³³ In this work, a gold NPs-based keypad lock was developed as shown in Figure 7. Red color of the gold NP dispersion was used as an initial state of the keypad lock. The three inputs EDTA, GSH and Hg²⁺ were designated as “E”, “G” and “H”, respectively. The output signal is defined as “Yes” (mimicking open state of the lock) when the value of A_{620}/A_{520} is higher than 0.5 and as “No” when it is lower than the threshold value. The addition of the inputs with different order, *i.e.*, HGE, HEG, EGH, EHG, GEH and GHE, resulted in distinct colorimetric response. For the input sequences of HGE and HEG, the values of A_{620}/A_{520} were lower than 0.5 since the deposition of the first added Hg²⁺ ions on the surface of gold NPs hindered the coordination of Hg²⁺ ions with the following added GSH.²³⁻²⁵ For the input sequence of EHG, the value of A_{620}/A_{520} was still lower than 0.5, attributed to coordination of the first added EDTA with the second added Hg²⁺, which prevented the interaction of Hg²⁺ with the finally added GSH. Due to the competitive binding of EDTA and GSH to the following added Hg²⁺ ions, the input sequences of EGH and GEH also resulted in A_{620}/A_{520} values lower than 0.5. In the case of GHE, the first added GSH tethered on the gold NP surface and interacted with the second added Hg²⁺ ions, the A_{620}/A_{520} value was as high as 1.4 due to the extensive aggregation of the NPs. Among the six sequences, only the correct sequence, GHE, resulted in the distinct red-to-blue color change and generated the “Yes” signal to mimic the opening state of the keypad lock. All other sequences presented A_{620}/A_{520} values lower than 0.5, thus producing the “No” signal. It was noted that in the GHE sequence, the third input E (EDTA) had little effect on the aggregation of the gold NPs. Further design and synthesis of polypeptide ligands that can interact with the NPs and metal ions in a cooperative and reversible manner would be beneficial for fully mimicking the function of the traditional keypad lock.

Conclusions

In summary, several logic gates (AND, OR, INHIBIT and sequential gate) and a keypad lock were fabricated here by taking advantage of the GSH-controlled dispersion and aggregation of gold NPs. The as-designed logic gates worked well under wide range of conditions and had a fast colorimetric response that can be easily observed by naked eyes. To the best of our knowledge, this is the first report to fabricate gold NPs-based logic gate by using the commercially available oligopeptides such as GSH. Considering the diversity of peptides, it is expected that precisely designed polypeptides may become alternative candidates of DNA oligomers and organic ligands in construction of NPs-based logic gates and devices.

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Notes and references

^a State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun 130012, P. R. China. Fax: +86-431-85168868; Tel: +86-431-85168185;

E-mail: wsyang@jlu.edu.cn.

Electronic Supplementary Information (ESI) available: [TEM and DLS measurements. The effect of NaCl on the response time of AND gate. The influence of input adding order on the logic output.]. See DOI: 10.1039/b000000x/

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