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Sensitive Detection of Glucose Based on Gold Nanoparticles Assisted Silver Mirror Reaction

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Experimental section

Materials and instruments

D-(+)-glucose was purchased from Sigma-Aldrich. And the glucose kit was obtained from Shanghai Rongsheng Biotech co., Ltd. The UV/Vis spectra and optical density were recorded by UV2450 spectrophotometer (Shimadzu) and microplate spectrophotometer (TECAN, Infinite[®]200 PRO), respectively. All other chemicals used in the experiment were analytical grade, and distilled water was used throughout the work.

Methods

Preparation of Ag(NH₃)₂OH (Tollen's reagent)

According to the previous work,¹ we placed 6 mL of silver nitrate solution (0.1 M) in a 50 mL tube, ammonia (15M) was added with stirring until the brown precipitate just dissolved. We added 3mL of potassium hydroxide (0.8 M) solution, and the brown precipitate reformed. Then ammonia was added to dissolve the precipitate. Then distilled water was used to reach the final volume of 25 mL. The solution of $Ag(NH_3)_2OH$ should be fabricated just before use and stored in the dark.

Preparation of the AuNPs

We prepared the AuNPs with diameter of 13 nm by the citrate-mediated reduction of $HAuCl_4$ according to the approach that was reported before.² The final concentration of the Au NPs is 10 nM.

Optimization of the experiments

We tested a series of concentrations of Ag $(NH_3)_2OH$ to optimize the conditions. The system contained 20 µL Au NPs (10 nM), 20 µL glucose (1 mM) in distilled water. Different volumes of the Ag $(NH_3)_2OH$ were allowed to reach a final volume of 200 µL. The concentration of the Ag $(NH_3)_2OH$ ranged from 0 mM to 3.6 mM. After 15min reaction at room temperature, the UV/vis spectrum of the solution was measured by UV/Vis spectrophotometer.

We optimized the concentration of the Au NPs in the system. We allowed 20 μ L glucose (1mM) and various volumes of 10 nM Au NPs into distilled water to reach the volume of 185 μ L. Then we added 15 μ L Tollen's reagent to reach the final volume of 200 μ L. The concentration of Au NPs was from 0.1 nM to 8 nM. After 15min at room temperature, we used UV/Vis spectrophotometer to measure the UV spectra of the solution.

Dynamic curve of the Au NPs assisted silver mirror reaction

20 μ L Au NPs (10 nM), 20 μ L glucose (1 mM) and 15 μ L Ag(NH₃)₂OH were added into distilled water to reach the final volume 200 μ L. We carried out the reaction at room temperature for 15 min ,then measured the absorbance at 410 nm of the solution by using micro plate spectrophotometer from 0 to 90 min at room temperature to obtain the dynamic curve of the reaction. Figure S3 shows the dynamic curve of the AuSMR.

Influence of the ion strength on AuSMR

We added 20 μ L glucose (1 mM) with different concentrations of NaCl ranging from 7.25 to 508 mM into the solution including 20 μ L Au NPs (10 nM), 145 μ L distilled water, 15 μ L Tollen's reagent. We performed the reaction for 15 min at room temperature, and then measured the absorbance at 410 nm with micro plate spectrophotometer.

Interference test

We tested some chemicals and biological samples that potentially interfered SMR including bovine serum albumin, goat serum, fetal bovine serum, sodium citrate, citric acid, formaldehyde and vitamin C. All the concentrations of these samples were 1% (w/v) in distilled water. We added 20 μ L the listed samples into the solution containing 20 μ L Au NPs (10 nM), 15 μ L Tollen's reagent and 145 μ L distilled water to examine their influence on the AuSMR. The reaction performed at room temperature for 15 min.

Detection of the glucose

We added 20 μ L glucose solution with a series of concentrations from 0 to 10 mM into the system containing 20 μ L Au NPs (10 nM), 145 μ L distilled water and 15 μ L Ag(NH₃)₂OH. The reaction also was performed for 15 min at room temperature. Then we monitored the UV/vis spectra of the solution by using UV/Vis spectrophotometer and the absorbance at 410 nm by micro plate spectrophotometer.

Detection of the glucose in mouse serum

After centrifuging at 3000 rpm for 15 min, we removed the precipitate from the whole blood of mouse to obtain the clear yellowish serum. We tested the concentration of glucose in the authentic serum with a commercial glucose kit, and different amount of glucose were added into serum to obtain the serum with different concentrations of glucose ranging from 4 mM to 23 mM. These sera were diluted with a ratio of serum to distilled water of 1:20. We allowed 20 µL diluted serum

into the solution containing 20 μ L Au NPs (10 nM), 15 μ L of Ag(NH₃)₂OH and 145 μ L distilled water. We carried out the reaction at 80 °C for 15 min. After the reaction, we measured the absorbance at 410 nm of the solution by using micro plate spectrophotometer.

Comparing the reducing ability between glucose and H_2O_2

We added 20 μ L glucose solution (1 mM) and 20 μ L H₂O₂ solution (1 mM) into the system containing 20 μ L Au NPs (10 nM), 145 μ L distilled water and 15 μ L Ag(NH₃)₂OH respectively. The reaction was performed for 15 min at room temperature. Then we monitored the UV/vis spectra of the solution by using UV/Vis spectrophotometer.



Fig.S1 A) Photographs and B) UV/Vis spectra of various concentrations of Ag(NH₃)₂OH ranging from 0 to 3.6 mM after AuSMR. The system contained 1 nM Au NPs and 1 mM glucose.



Fig.S2 A) Photographs and B) UV/Vis spectra of various concentrations of AuNPs ranging from

0.1 nM to 8 nM after AuSMR. The system contained 1.8 mM Ag(NH₃)₂OH and 1 mM

glucose.



Fig. S3 Dynamic curves of the Au NPs assisted silver mirror reaction. The absorbance at 410 nm was measured at 1 min, 3 min, 10 min, 15 min, 20 min, 30 min, 45 min, 60 min and 90 min respectively. The system contained 1.8 mM Ag(NH₃)₂OH, 1 nM Au NPs and 1 mM glucose.



Fig.S4 Influence of the ion strength on AuSMR. "1mM glucose" represents there is no salt in the solution. The absorbance of the solution with 145 mM NaCl (equals to the concentration of NaCl in physiological conditions) is shown by the arrow. The system contained 1.8 mM Ag(NH₃)₂OH and 1 nM Au NPs, and the absorbance at 410 nm was measured.



Fig.S5 The absorbance after AuSMR of interference test. All the concentrations of chemicals and biomolecules used above were 1% (w/v). "BSA" represents that there is only 1% BSA in AuSMR without glucose. The system contained 1.8 mM Ag(NH₃)₂OH, 1 nM Au NPs, and the absorbance at 410 nm was measured.



Fig.S6 The calibration curve of different concentrations of standard glucose samples with kit. The error bars represent the standard deviation of three measurements. The reaction performed at 37 °C for 15 min. The calibration curve was Y=0.0346X+0.0407, R²=0.9986.The absorbance at 505 nm of the serum (dilution ratio 1:10) with the kit was 0.0546. Thus the concentration of glucose in original mouse serum was about 4 mM.



Fig.S7 Comparing the reducing ability of glucoses and H₂O₂ at the same concentration (1 mM) in AuSMR system. The system contained 1 nM Au NPs, 1.8 mM Ag(NH₃)₂OH, 1 mM glucose (or 1 mM H₂O₂).



Fig.S8 (A)The TEM photos of AuNPs and (B) Au core-Ag shell NPs after AuSMR.

References

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