

Supporting information

Highly sensitive and facile colorimetric detection of glycidyl azide polymer based on propargylamine functionalized gold nanoparticles using click chemistry

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Experimental section

Chemicals and Apparatus. Copper(II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and ascorbic acid (AA) were purchased from Aladdin, Ltd. Sodium citrate, gold(III) chloride hydrate (HAuCl_4), phenol formaldehyde resin, polyvinyl pyrrolidone, carboxymethyl cellulose, polyvinyl alcohol, and gelatin were obtained from Sinopharm Chemical Reagent Co.,Ltd. (Shanghai, China). PEO-PPO-PEO triblock copolymer (P123), and ethylene-vinyl acetate copolymer (EVA) were purchased from Sigma-Aldrich. GAP (3430 g/mol) was purchased from Liming Research Institute of Chemical Industry (Luoyang, China). All the aqueous solutions were prepared with ultrapure water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$) from a Millipore Milli-Q system.

The morphology and size of the AuNPs were characterized using transmission electron microscopy (TEM). UV-vis absorption spectra were recorded with a UV-vis spectrophotometer (Shimadzu UV-1800, Japan). Fourier transform infrared (FT-IR) spectra were obtained on a TENSOR spectrophotometer (Bruker, Germany).

Synthesis of AuNPs. AuNPs were synthesized through classical citrate-mediated reduction of HAuCl_4 ^{S1}. Briefly, a stirred aqueous solution of HAuCl_4 (100 mL, 0.01%) was heated to boiling, and then sodium citrate (1%, 4 mL) was added quickly under vigorous stirring, producing a distinct color change from pale yellow to deep red. Finally, the deep red solution was cooled down to room temperature. The average diameter of the as-prepared AuNPs was about 13 nm, and the solution concentration was estimated to be 0.98 nM by the Beer's law, using an extinction coefficient of ca. $6 \times 10^8 \text{ M}^{-1} \text{ cm}^{-1}$ S1.

Synthesis of propargylamine functionalized AuNPs. Propargylamine functionalized AuNPs (ProAuNPs) were prepared via the Au-N covalent interaction of AuNPs and propargylamine, which is similar to the reported method for preparation of propargylamine functionalized silver nanoparticles^{S2}. Typically, 7 mL of 10 μM propargylamine aqueous solution was added to 93 mL AuNPs solution and then reacted with three hours under vigorous stirring at room temperature.

Afterwards, the mixture solution was centrifuged at 12500 rpm for 15 min and the precipitates were redispersed with ultrapure water and stored at 4°C until use.

Process of the colorimetric sensor for the detection of GAP. The detection of GAP was performed under the following procedures. Firstly, 1 mL of ProAuNPs was mixed with 1 mL of ultrapure water and 0.3 mL of 1 mM $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ aqueous solution. Secondly, 0.3 mL of GAP solution with a final different concentration ranging from 0 to 6 $\mu\text{g/mL}$, and 0.4 mL of 4 mM ascorbic acid were successively added into the above mixture solution. Then, the above mixture solution was incubated for 1 h at 40 °C. After cooling down to room temperature, the UV-vis absorption spectra of mixture solution were collected on a UV-vis spectrophotometer.

Detection of GAP in real sample. Lake water was collected from Center Lake of Southwest University of Science and Technology. Before being used for analysis, the lake water sample was diluted with ultrapure water at the ratio of 1:10. GAP solutions with different concentrations were spiked into the diluted lake water sample. Afterwards, GAP concentration of each sample was also measured under the reaction conditions mentioned above.

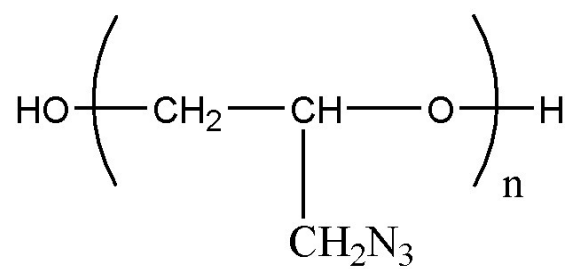


Fig. S1 The molecular structure of GAP.

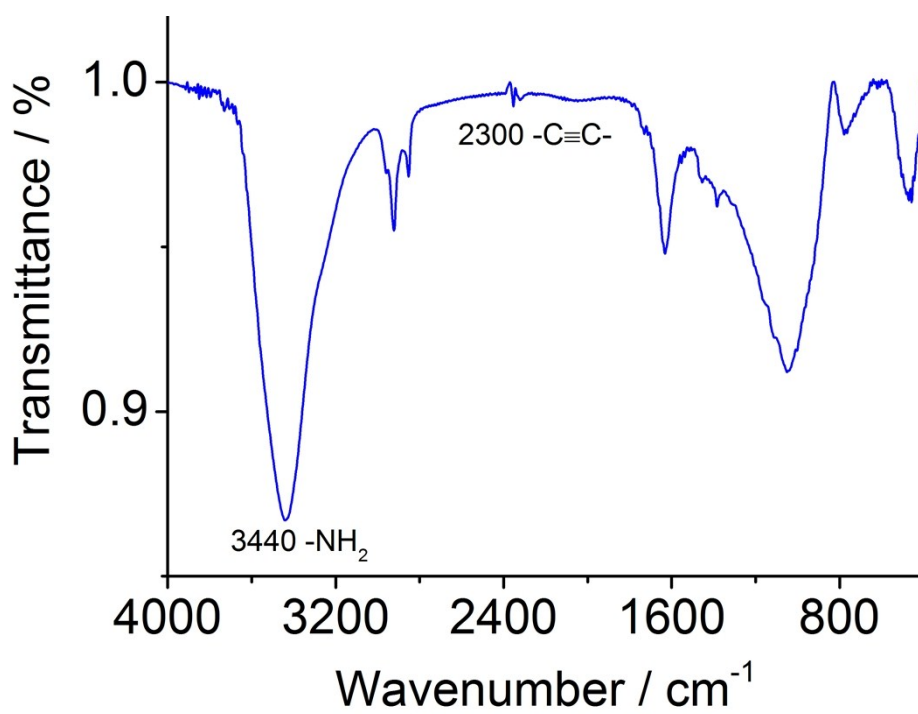


Fig. S2 FT-IR spectrum of ProAuNPs.

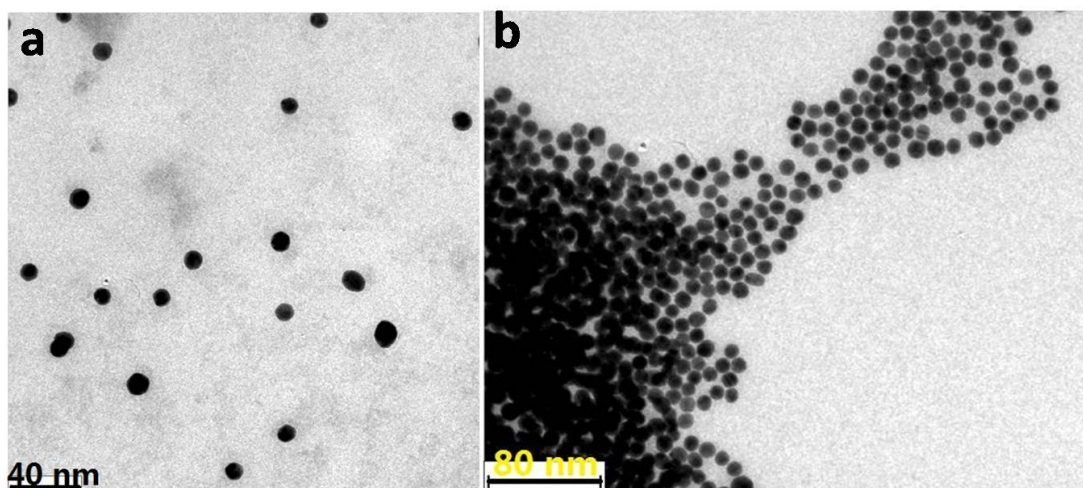


Fig. S3 TEM images of the mixtures with different components: (a) ProAuNPs, ascorbic acid, and Cu(II); (b) ProAuNPs, ascorbic acid, Cu(II), and GAP (6 $\mu\text{g}/\text{mL}$).

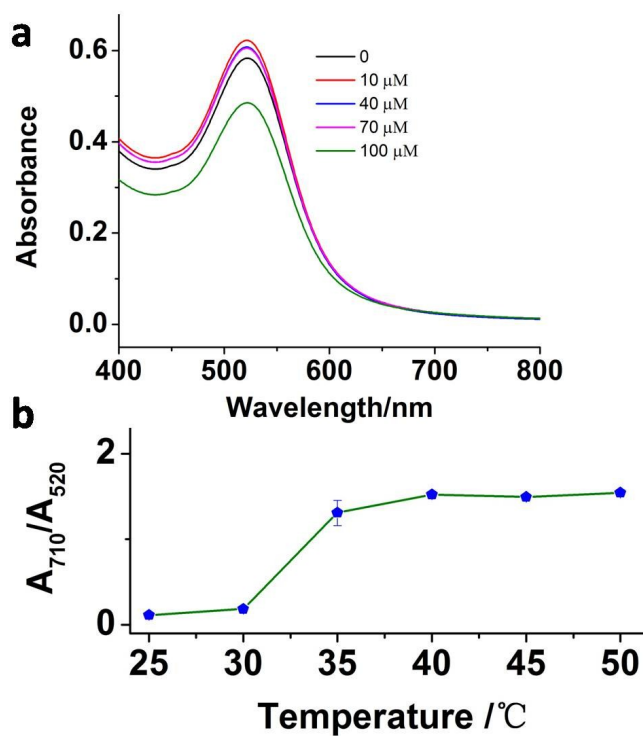


Fig. S4 (a) UV-vis spectra of AuNPs in the presence of different concentrations of propargylamine. (b) Effect of reaction temperature on the absorbance ratio (A_{710}/A_{520}) of the sensing system.

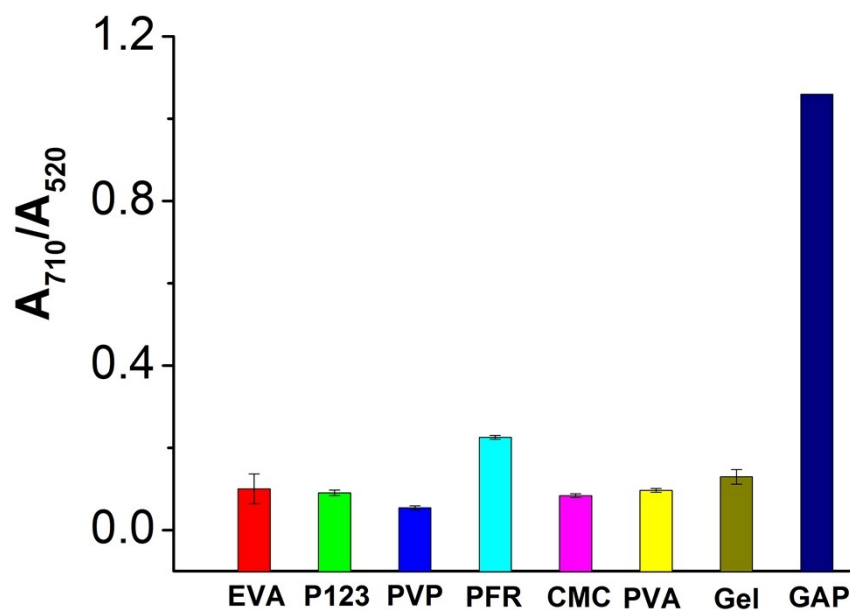


Fig. S5 The selectivity of the colorimetric sensor toward EVA, P123, PVP, PFR, CMC, PVA, Gel, and GAP in lake water. The concentrations of GAP and other substances are 6 $\mu\text{g/mL}$ and 60 $\mu\text{g/mL}$, respectively.

Table S1 Detected results and recoveries of GAP in lake water samples

| Samples | Added ($\mu\text{g/mL}$) | Found ($\mu\text{g/mL}$) | Recoveries (%) |
|--------------|----------------------------|----------------------------|----------------|
| Lake water 1 | 0.1 | 0.095 | 95 |
| Lake water 2 | 2 | 1.96 | 98 |
| Lake water 3 | 6 | 5.94 | 99 |

S1 Y. He and H. Cui, *Biosens. Bioelectron.*, 2013, **47**, 313.

S2 H. F. Zhao, R. P. Liang, J. W. Wang and J. D. Qiu, *Biosens. Bioelectron.*, 2015, **63**, 458.