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

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A highly sensitive and facile colorimetric sensor for glycidyl azide polymer explosive was developed based on propargylamine functionalized gold nanoparticles using click chemistry.

The development of high sensitive and facile assays for various explosives has gained a great attention in terms of ecological environment, national security, and human health¹. Traditional analytical technologies, such as gas chromatography (GC), high performance liquid chromatography (HPLC), gel permeation chromatography (GPC), X-ray imaging, and ion mobility mass spectrometry, have been developed for the detection of explosives over the years²⁻⁴. However, these methods need bulky equipments and complicated sample pretreatment, making them unsuitable for rapid on-site detection of explosives.

For this reason, extensive efforts have been devoted to develop several chemsensors. To date, fluorescent, colorimetric, and electrochemical chemsensors have been fabricated for the detection of explosives⁵⁻⁷. Among them, colorimetric chemsensors are more promising than others due to their simple instrumentation, cost-efficiency, and high sensitivity. Particularly, gold nanoparticles (AuNPs)-based colorimetric sensors have been widely investigated because the extinction coefficient of AuNPs is several orders of magnitude larger than that of traditional organic chromophores. Some common small-molecule explosives such as 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT), cyclotetramethylene tetranitramine (HMX), and hexogen (RDX) have been sensitively detected based on the AuNPs-based colorimetric sensors⁸⁻¹⁰. For example, Mao and coworkers utilize the donor-acceptor interaction between TNT and cysteamine at the AuNPs/solution interface to develop a simple assay for the direct colorimetric visualization of TNT down to the picomolar level⁸.

Despite these progresses, there is still a strong demand for AuNPs-based colorimetric sensors to be used for the detection of

other explosives. Glycidyl azide polymer (GAP) is a macromolecular explosive (Fig. S1)¹¹. Compared with common small-molecule explosives, the mechanical sensitivity of GAP is apparently high, and it is easily exploded under impact and friction conditions¹², which means that GAP is more dangerous than small-molecule explosives. Also, GAP has been considered as an environmental contaminant¹³. Nevertheless, to the best of our knowledge, there is no report on the chemsensor for the detection of GAP.

Herein, we report a facile and highly sensitive chemsensor for the detection of GAP by propargylamine functionalized AuNPs (ProAuNPs) using click chemistry for the first time. The presence of Cu(I) as the catalyst can promote the cycloaddition reaction between GAP and propargylamine functionalized AuNPs in click chemistry based on Huisgens reaction, which leads to the aggregation of AuNPs, causing a color change of AuNPs solution. This phenomenon allows the naked eye to assay for the GAP even at 0.1 μ g/mL concentration. In addition, the potential application of the chemsensor to real sample (lake water) was also explored.

ProAuNPs were prepared via the Au-N covalent interaction of AuNPs and propargylamine (Fig. 1a)¹⁴. The successful formation of ProAuNPs was characterized using FT-IR spectroscopy. As shown in Fig. S2, ProAuNPs exhibit the characteristic vibrational frequencies of propargylamine at 3440 and 2300 cm^{-1} , which are attributed to the N-H and C \equiv C stretching vibrations, respectively. Moreover, the characteristic absorption bands of citrate at 2950 (C-H stretching vibration), 1630 (C=O stretching vibration), and 1050 cm^{-1} (C-O stretching vibration) are also observed, indicating that citrate exists on the surface of AuNPs. The results demonstrated that propargylamine was adsorbed on the surface of AuNPs.

The principle of the AuNPs-based colorimetric sensor for GAP is illustrated in Fig. 1b. In the absence of GAP, ProAuNPs exhibit a good stability and dispersion in the solution due to the strong electrostatic repulsion of citrate between each other. However, in the presence of GAP, the cycloaddition reaction between GAP and ProAuNPs is triggered via Cu(I) that is formed from the redox reaction of Cu(II) and ascorbic acid. The occurrence of the cycloaddition reaction caused the aggregation of ProAuNPs and provoked a red-to-blue color change of the solution. The degree of aggregation of ProAuNPs was directly related to the addition of GAP

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concentration, thus, this principle can be utilized for the detection of GAP via the change in the UV-vis spectrum of ProAuNPs dispersion.

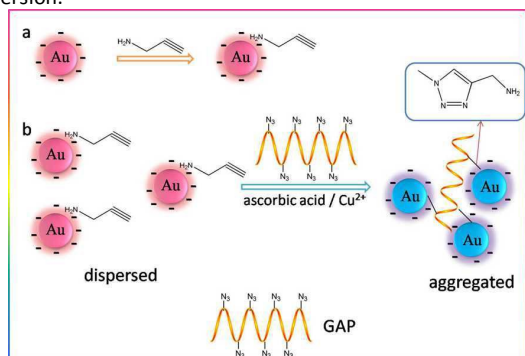


Fig. 1 (a) Preparation of ProAuNPs. (b) Sensing mechanism of AuNPs-based colorimetric sensor for GAP using click chemistry.

UV-vis absorption spectroscopy and TEM characterizations were used to verify the presumption. As displayed in Fig. 2, the dispersion consisted of ProAuNPs, ascorbic acid, and Cu(II) shows a typical surface plasmon resonance (SPR) band at 520 nm and appears red in color. When 6 $\mu\text{g/mL}$ GAP was added into the dispersion, the color of the dispersion changed from red to blue, and a new SPR band at 710 nm was observed, indicating that the aggregation of ProAuNPs occurred. The aggregation of AuNPs was demonstrated by TEM. As shown in Fig. S3, without GAP, ProAuNPs are well dispersed. However, in the presence of 6 $\mu\text{g/mL}$ GAP, ProAuNPs aggregate into larger clusters, which is accorded in the UV-vis spectra results mentioned above.

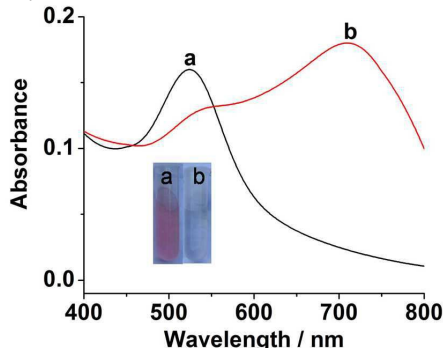


Fig. 2 UV-vis spectra of the mixtures with different components: (a) ProAuNPs, ascorbic acid, and Cu(II); (b) ProAuNPs, ascorbic acid, Cu(II), and GAP (6 $\mu\text{g/mL}$) (inset: corresponding photographs).

The amount of propargylamine immobilized on the surface of AuNPs is an important factor for Huisgens reaction. If the concentration of propargylamine is not high enough, Huisgens reaction can not proceed effectively. Nevertheless, if the concentration of propargylamine is too high, it can generate the aggregation of AuNPs. As shown in Fig. S4a, the absorbance of AuNPs at 520 nm slightly increases with the increasing of propargylamine concentration in the range of 0-70 μM , and decreases when the concentration of propargylamine exceeds 70 μM , suggesting that AuNPs are not stable in the presence of high concentration of propargylamine. Taking into account the stability of AuNPs, 70 μM of propargylamine was chosen for the following

experiments. The reaction temperature is another important parameter that affects the absorption signal. Fig. S4b displays the effect of reaction temperature on the absorbance ratio (A_{710}/A_{520}). From Fig. S4b, the A_{710}/A_{520} increases with increasing reaction temperature from 25 $^{\circ}\text{C}$ to 40 $^{\circ}\text{C}$ and reaches a plateau at 40 $^{\circ}\text{C}$. Therefore, the reaction temperature was maintained at 40 $^{\circ}\text{C}$ for the following experiments.

Under the optimized experimental conditions, the colorimetric sensor was used for the detection of GAP. Fig. 3a reveals the UV-vis absorption spectra of the sensing system at different GAP concentrations. As the increasing of the concentration of GAP, the UV-vis absorption curves exhibit red-shift, and a peak appears at 710 nm. The absorbance ratio (A_{710}/A_{520}) gradually increased as the GAP concentration increased. The calibration plot shows a good linear relationship between the logarithmic value of A_{710}/A_{520} and GAP concentration ranging from 0.1 to 6 $\mu\text{g/mL}$. The linear regression equation is $\text{Log } A_{710}/A_{520} = 0.22 C - 1.0$ with a correlation coefficient of 0.995 (Fig. 3b), where C is the concentration of GAP. The detection of limit (LOD) is calculated to be 0.05 $\mu\text{g/mL}$ based on a signal-to-noise ratio of 3. This LOD is much lower than that of traditional GPC-based method (0.5 mg/mL)¹⁵. More interestingly, the color change of the sensing system from red to blue can be directly observed by the naked eye (Fig. 3c). The LOD by the naked eye is as low as 0.1 $\mu\text{g/mL}$.

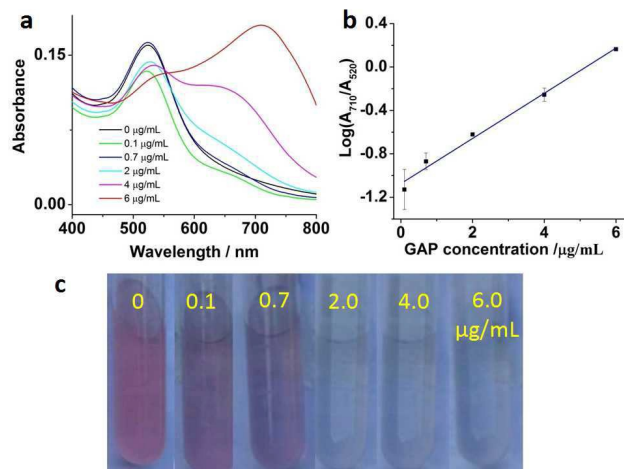


Fig. 3 (a) UV-vis spectra of the mixture consisted of ProAuNPs, ascorbic acid, Cu(II) in the presence of various concentrations of GAP (0-6 $\mu\text{g/mL}$). (b) Calibration curve between the logarithm of the absorbance ratio (A_{710}/A_{520}) and the GAP concentrations. (c) The photographs of the sensing system in the presence of different concentrations of GAP.

In order to evaluate the selectivity of the colorimetric sensor, the UV-vis absorption responses of the sensing system were measured for other common macromolecules such as ethylene-vinyl acetate copolymer (EVA), PEO-PPO-PEO triblock copolymer (P123), polyvinyl pyrrolidone (PVP), phenol formaldehyde resin (PFR), carboxymethyl cellulose (CMC), polyvinyl alcohol (PVA), and gelatin (Gel). The anti-interference experiment was carried out by determining a solution containing 6 $\mu\text{g/mL}$ GAP and 60 $\mu\text{g/mL}$ interfering substances. As shown in Fig. 4, only the presence of GAP leads to a significant absorbance ratio, while other interfering substances cause a very weak absorbance ratio. The results reveal

that 10-fold other tested macromolecules do not interfere with the detection of GAP, indicating that the developed colorimetric sensor has a good selectivity for the detection of GAP. The good selectivity for GAP detection is derived from the high specificity of Huisgens reaction.

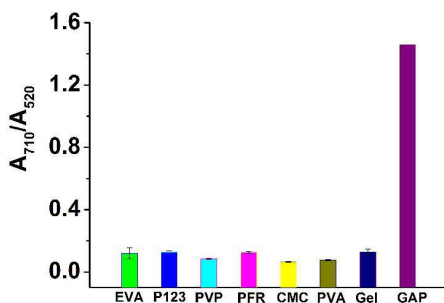


Fig. 4 The selectivity of the colorimetric sensor toward EVA, P123, PVP, PFR, CMC, PVA, Gel, and GAP. The concentrations of GAP and other substances are 6 $\mu\text{g/mL}$ and 60 $\mu\text{g/mL}$, respectively.

The stability of the developed colorimetric sensor was also investigated by determining the absorption response of 6 $\mu\text{g/mL}$ GAP for one month. The absorbance ratio (A_{710}/A_{520}) exhibited no apparent change after having been stored in darkness for one month at 4 °C. The results demonstrated that the developed colorimetric sensor was very stable. The reproducibility and precision of the developed colorimetric sensor were examined at 0.7, 2, 6 $\mu\text{g/mL}$ GAP for five times. The relative standard deviations (RSDs) of the intra-assay were 8.8%, 1.1%, and 0.8%, and the RSDs of the inter-assay with different batches were 9.5%, 2.3%, and 1.5% at the corresponding concentrations. Accordingly, these results demonstrate that the developed colorimetric sensor had an acceptable reproducibility and precision.

To monitor the practical application of the colorimetric sensor, lake water samples were spiked with 0.1, 2, 6 $\mu\text{g/mL}$ GAP and detected according to the sensing system. As shown in Table S1, the recoveries range from 95% to 99%, indicating acceptable accuracy. Moreover, the selectivity of this sensor in lake water was also investigated. As shown in Fig. S5, similar to the results obtained in ultrapure water, only GAP produced an evidently increase in the value of the absorbance ratio (A_{710}/A_{520}), demonstrating that the sensor also had a good selectivity in lake water. Therefore, the colorimetric sensor is suitable for GAP detection in environmental water samples.

In summary, we have developed a colorimetric sensor for detecting macromolecular explosive GAP in aqueous solution using Cu(I)-catalyzed click chemistry between GAP and propargylamine functionalized AuNPs. The colorimetric sensor combines the high specificity of Huisgens reaction to GAP with the advantages of functionalized gold nanoparticles to allow for sensitive detection of GAP. Moreover, the naked-eye detection of GAP is not reported, and our developed colorimetric sensor is the first time to realize the detection of GAP by the naked eye. Significantly, the developed sensor with simplicity, less instrumental demands, and high selectivity has been successfully applied for the detection of GAP in real samples. These above-mentioned advantages make us believe

that the developed colorimetric sensor holds great potential application in monitoring GAP and GAP-related explosives. It should also be noted that the sensor had a relatively narrow linear range (0.1–6 $\mu\text{g/mL}$). We will attempt to overcome the disadvantage by using other functionalized gold nanoparticles. Further work is ongoing.

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Notes and references

- Z. Hu, B. J. Deibert and J. Li, *Chem. Soc. Rev.*, 2014, **43**, 5815.
- F. Xiao, K. Wang, F. B. Wang and X. H. Xia, *Anal. Chem.*, 2015, **87**, 4530.
- M. Rong, L. Lin, X. Song, T. Zhao, Y. X. Zhong, J. W. Yan, Y. Wang and X. Chen, *Anal. Chem.*, 2014, **87**, 1288.
- J. Ye, L. Zhao, R. F. Bogale, Y. Gao, X. Wang, X. Qian, S. Guo, J. Zhao and G. Ning, *Chem. Eur. J.*, 2015, **21**, 2029.
- Y. Guo, X. Feng, T. Han, S. Wang, Z. Lin, Y. Dong and B. Wang, *J. Am. Chem. Soc.*, 2014, **136**, 15485.
- S. Zhu, X. Zhang, J. Cui, Y. E. Shi, X. Jiang, Z. Liu and J. Zhan, *Analyst*, 2015, **140**, 2815.
- D. Lin, H. Liu, K. Qian, X. Zhou, L. Yang and J. Liu, *Anal. Chim. Acta*, 2012, **744**, 92.
- Y. Jiang, H. Zhao, N. Zhu, Y. Lin, P. Yu and L. Mao, *Angew. Chem. Int. Ed.*, 2008, **120**, 8729.
- R. Bharadwaj and S. Mukherji, *Sensor. Actuat. B: Chem.*, 2014, **192**, 804.
- A. e. Üzer, Z. Can, I. I. Akın, E. Erçağ and R. a. Apak, *Anal. Chem.*, 2013, **86**, 351.
- T. Wang, S. Li, B. Yang, C. Huang and Y. Li, *J. Phys. Chem. B*, 2007, **111**, 2449.
- M. Laviolette, M. Auger and S. Desilets, *Macromolecules*, 1999, **32**, 1602.
- M. Talawar, R. Sivabalan, T. Mukundan, H. Muthurajan, A. Sikder, B. Gandhe and A. S. Rao, *J. Hazard. Mater.*, 2009, **161**, 589.
- H. F. Zhao, R. P. Liang, J. W. Wang and J. D. Qiu, *Biosens. Bioelectron.*, 2015, **63**, 458.
- S. Brochu and G. Ampleman, *Macromolecules*, 1996, **29**, 5539.