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Graphical Abstract

Colorimetric detection of quaternary ammonium surfactants using citrate-stabilized gold nanoparticles (Au NPs)
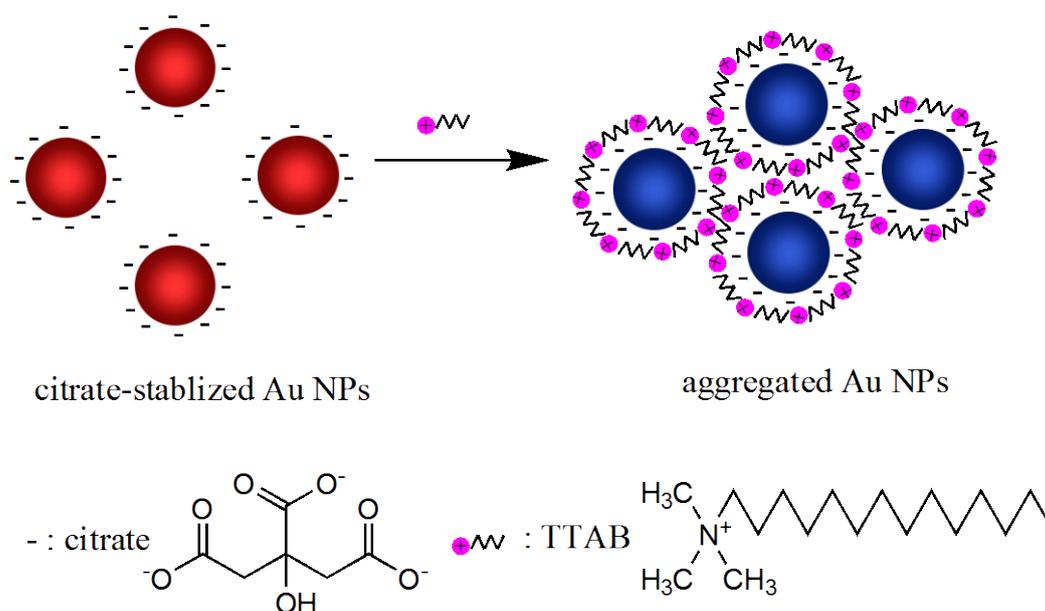
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citrate-stablized Au NPs   aggregated Au NPs

- : citrate   : TTAB

Based on the hydrophobic effect inducing the aggregation of Au NPs, a rapid and low-cost colorimetric method for detection of quaternary ammonium surfactants using citrate-stabilized AuNPs was developed.

Journal Name

Colorimetric detection of quaternary ammonium surfactants using citrate-stabilized gold nanoparticles (Au NPs)

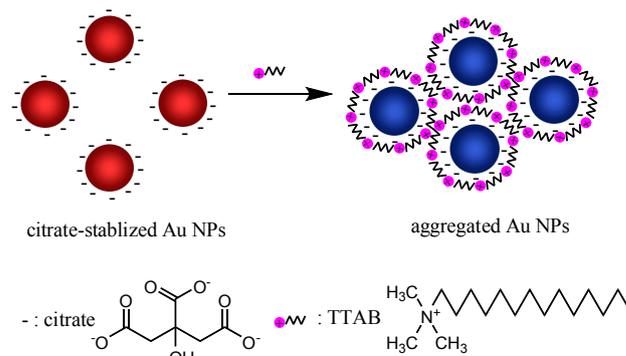**Li-Qing Zheng, Xiao-Dong Yu,* Jing-Juan Xu and Hong-Yuan Chen**

A rapid and low-cost colorimetric method for detection of quaternary ammonium surfactants using citrate-stabilized AuNPs based on hydrophobic effect was developed. The LODs of different surfactants ranged from 0.5 µM to 5 µM.

10 The quaternary ammonium surfactants are widely applied in industry, especially in pharmacy. For instance, Myristyltrimethylammonium bromide (TTAB) is used as one of the major components of eye drops. While TTAB may cause an allergic reaction in some sensitive people. On the other hand, the
15 surfactants can lead to environmental pollution when they are deposited on land or into water systems[1]. Therefore, establishing a sensitive method to detect quaternary ammonium surfactants is very important for environmental protection and human health. Various detection methods have been reported, such as reversed-
20 phase high-performance liquid chromatographic (RP-HPLC)[2], gas chromatography-mass spectrometry (GC-MS)[3], capillary electrophoresis (CE)[4], two-phase titration[5], etc. However, these methods require expensive equipments and sophisticated sample processing, which lead to quite inconvenient for on-site detection.
25 On the contrary, in colorimetric method, target molecule can be monitored by naked eyes sensitively without instrument, so colorimetric method is extremely low-cost and has attracted much attention[6].

Recently, noble metal nanoparticles have played vital roles
30 in both chemistry and biochemistry because of their inherently robust chemical properties[7], such as special size-dependent optical properties. For example, the color of dispersed Au NPs solution is red while the highly aggregated Au NPs solution turns out to be blue[8]. Based on this phenomenon, the Au NPs
35 are widely used for the colorimetric detections of various targets, including cells[9], proteins[10], DNA[11], small molecules[12] and metal ions[8b,13], etc. Another metal nanoparticles, Ag NPs are also widely applied in the colorimetric analysis[14]. However, the Au NPs have some intrinsic advantages over Ag
40 NPs. For example, the Au NPs possess much better stability than Ag NPs due to the easily surface oxidation of the

55 Ag NPs[15]. Furthermore, the extraordinarily high extinction coefficient of Au NPs enables the colorimetric assay to be extremely sensitive.

There are various mechanisms of inducing the aggregation of metal nanoparticles that have been reported, such as
60 electrostatic interaction between negative ion and positive ion[16], complexation with ligand[17], antibody-antigen associations[18], thiolated or disulfide modified ligands[19], streptavidin-biotin binding[20], etc. Recently, our group has reported that the aggregation of Ag NPs induced by the hydrophobic effect[21].
65 Based on the strategy, herein, a rapid and low-cost colorimetric method for detection of quaternary ammonium surfactants using citrate-stabilized Au NPs was developed. The strategy is illustrated in Scheme 1. Quaternary ammonium surfactants were adsorbed onto the surface of citrate-stabilized Au NPs by
70 electrostatic attraction and the surface of Au NPs became hydrophobic. Then Au NPs aggregated through hydrophobic interaction. Compared to the Ag NPs, the red-to-blue color change resulting from the aggregation of the Au NPs is more remarkable than the yellow-to-colorless change of Ag NPs
75 solution. Therefore, the Au NPs should be more sensitive to the cationic surfactants. What's more, the UV/Vis spectra of the Au NPs solution response to the surface plasma resonance changes are completely different from Ag NPs solution.

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† Electronic Supplementary Information (ESI) available. See DOI: 10.1039/b000000x/

80 **Scheme 1** Schematic mechanism for TTAB inducing the aggregation of citrate-stabilized Au NPs.

The Au NPs solution was synthesized by the classical reaction of HAuCl$_4$ reduced by sodium citrate (see ESI†)[13c]. As the TEM images showed in Fig.1, the size of the dispersed Au NPs was ca.17 nm (Fig 1A), while after the addition of 10 μM TTAB, the Au NPs distinctly aggregated (Fig. 1B). The absorbance ratio A$_{650}$/A$_{525}$ of Au NPs solutions with addition of 1 μM TTAB under different pH conditions were shown in Fig. S1 (ESI†). It can be seen that the absorbance ratio A$_{650}$/A$_{525}$[8b] reached maximum value at pH 3, which indicated the most aggregation of Au NPs. In the 10^{-3}M HNO$_3$ solution, the Au NPs showed the most sensitive response to TTAB, therefore 10^{-3}M HNO$_3$ was chosen as the optimal experiment condition. As shown in Fig. 2A, the color of Au NPs solution changed from red to purple upon the addition of 10 μM TTAB. The color change of the Au NPs solution in the presence of TTAB was also monitored by UV/Vis spectroscopy (Fig. 2B). When 10 μM TTAB was added to the Au NPs solution, the UV spectra of the Au NPs solution showed that the plasmon band at 525 nm significantly decreased and an absorption peak at 650 nm emerged, indicating the aggregation of the Au NPs.
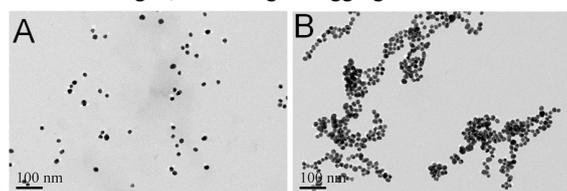

Fig. 1 TEM images of citrate-stabilized Au NPs (A) before and (B) after addition of TTAB (10 μM).
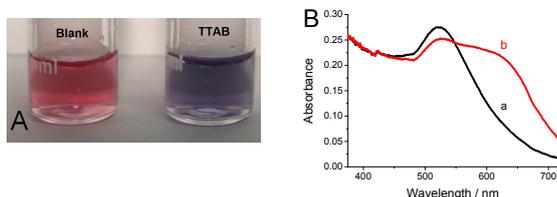

Fig. 2 (A) The color change of the Au NPs solution (10^{-3}M HNO$_3$) with the addition of 10 μM TTAB. (B) the corresponding absorption spectrum of the Au NPs solution (10^{-3}M HNO$_3$) before (a) and after (b) the addition of 10 μM TTAB.

The selectivity of citrate-stabilized Au NPs was evaluated with the addition of various surfactants. As can be seen in Fig.3, anionic and neutral surfactants could not induce the aggregation of Au NPs according to the strategy. The influence of NaClO$_4$, Na$_2$SO$_4$, Na$_3$PO$_4$, NaNO$_3$, NaCl and Na$_2$SO$_3$ on the aggregation of Au NPs was also investigated. The results showed that 10^{-2} M ClO$_4^-$, SO4^{2-} and 5×10^{-2} M PO$_4^{3-}$, NO$_3^-$, Cl$^-$, SO$_3^{2-}$ could interfere with the detection (see Fig. S2 in ESI†).
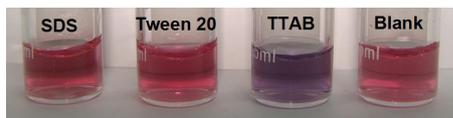

Fig. 3 Colorimetric response of Au NPs solution (10^{-3}M HNO$_3$) upon the addition of 10 μM various surfactants.

The sensitivity of Au NPs for colorimetric detection of TTAB was evaluated and the result was shown in Fig. 4. With increase in the concentration of TTAB, the color of the Au NPs solution changed from red to blue then finally to red purple. The LOD of TTAB is 3 μM. The color changes were also monitored by UV/Vis spectroscopy. The ratio of absorbance intensities at 650 and 525 nm (A$_{650}$/A$_{525}$) was used to assess the degree of Au NPs aggregation. The larger value of the ratio indicates the more aggregation of Au NPs[6b,8b]. As shown in Fig. 4B, increasing the concentration of TTAB, A$_{650}$/A$_{525}$ increased rapidly to maximum and remained unchanged when the concentration of TTAB was in the range of 3-7 μM, then decreased gradually. This could be ascribed to the different aggregation degree of Au NPs. Increasing concentration of TTAB, the aggregation of Au NPs intensified and then reached to saturation. Further increasing the concentration of TTAB, the Au NPs tended to redisperse and this could be ascribed to the reversal of surface charge of Au NPs[22].
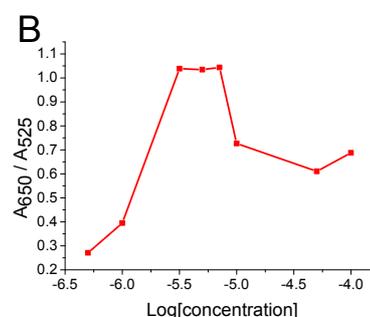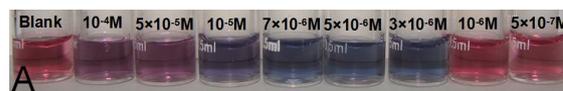

Fig. 4 (A) Colorimetric visualization of TTAB using citrate-stabilized Au NPs. TTAB concentrations varied from 5×10^{-7} M to 10^{-4} M. (B) The plot of A$_{650}$/A$_{525}$ against log[TTAB]. The concentration of TTAB corresponded to 5×10^{-7} M, 10^{-6} M, 3×10^{-6} M, 5×10^{-6} M, 7×10^{-6} M, 10^{-5} M, 5×10^{-5} M and 10^{-4}M TTAB, respectively.

The cationic surfactant had many homologs with different length of the alkyl chain. The response of Au NPs upon the addition of different cationic surfactants including Dodecyl Trimethyl Ammonium Bromide (DTAB), Benzalkonium Bromide (BZKB) and Cetrimonium Bromide (CTAB) were investigated. The results could be seen in Fig.5. The LODs of these cationic surfactants ranged from 0.5 μM to 5 μM.
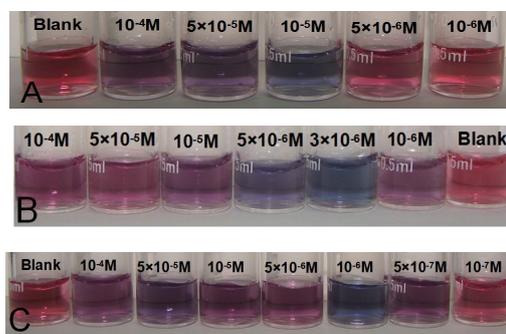

Fig. 5 The visual color change of the Au NPs solution (10^{-3}M

HNO₃) with the addition of a series of concentrations of different quaternary ammonium surfactants. (A) DTAB; (B) BZKB; (C) CTAB.

To verify the utility of the colorimetric method, BZKB in the disinfectant residual sample was detected. As shown in Fig. 6, the color of Au NPs solution clearly changed from red to blue than to red purple upon the addition of sample with different dilution ratios. According to the color change of Au NPs solution, the concentration of BZKB was approximately 2×10^{-4} M in the disinfectant residual sample. The detection of BZKB in disinfectant residual sample by RP-HPLC was also investigated in order to verify the accuracy of the colorimetric method. The result was shown in Fig. S3 and Fig. S4 (ESI †), The concentration of BZKB was 2.267×10^{-4} M determined by RP-HPLC. The result was basically consistent with that of the colorimetric method. It also suggested that this simply colorimetric strategy could be applied to the semiquantitative analysis of BZKB.
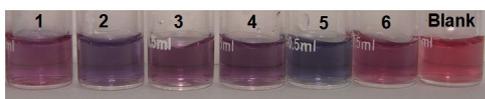

Fig. 6 Colorimetric response of the Au NPs (10^{-3}M HNO₃) upon the addition of different dilution multiple of the disinfectant residual sample containing BZKB. In the picture, 1-6 corresponded to the sample dilution multiple of 2, 4, 20, 40, 66 and 200 times, respectively.

In conclusion, based on the aggregation of Au NPs induced by the hydrophobic effect, a rapid, sensitive and low-cost colorimetric method for detection of quaternary ammonium surfactants using citrate-stabilized AuNPs was developed. The colorimetric method was successfully used to detect BZKB in the disinfectant residual sample. With intrinsic advantages of colorimetric method such as simplicity and sensitivity, it is potential to be applied in the on-site detection of cationic surfactants in the environment.

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