

The Aggregation of Destabilized Ag Triangular Nanoplates and Its Application in Detection of Thiram Residues

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The Ag-S bond was characterized by SERS spectrum, as shown in Figure S1. One can clearly see the Ag-S mode at 233 cm^{-1} , which indicates the formation of Ag-S bond [1].

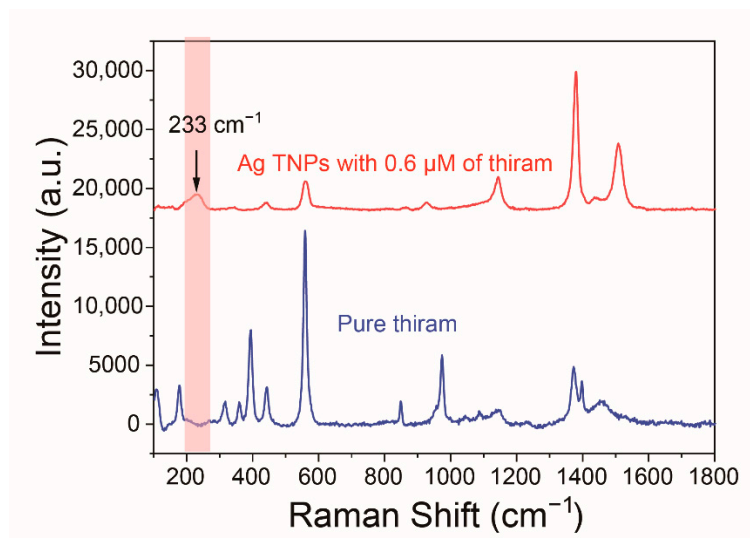


Figure S1. The Raman properties of Ag TNP with $0.6\text{ }\mu\text{M}$ of thiram and the pure thiram. The main absorption peak of the Ag TNPs is at 700 nm .

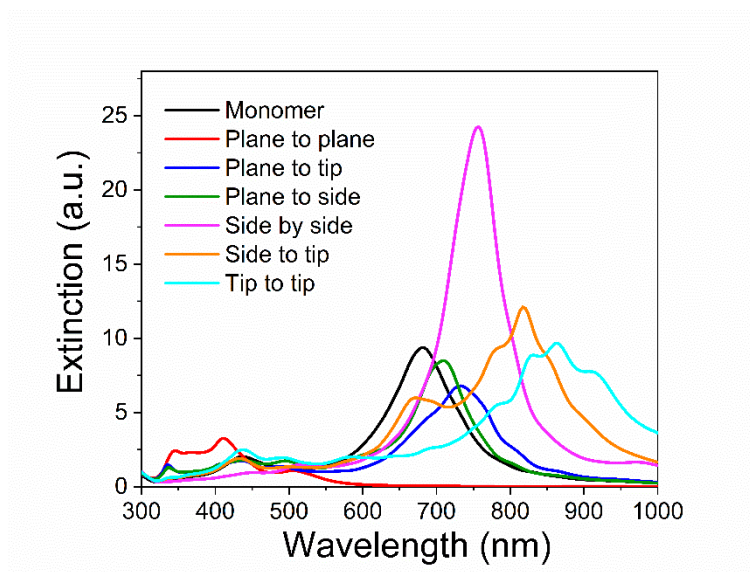


Figure S2. The extinction spectra of the monomer and the six assembly forms of Ag TNPs (the polarization was set along the coupling direction).

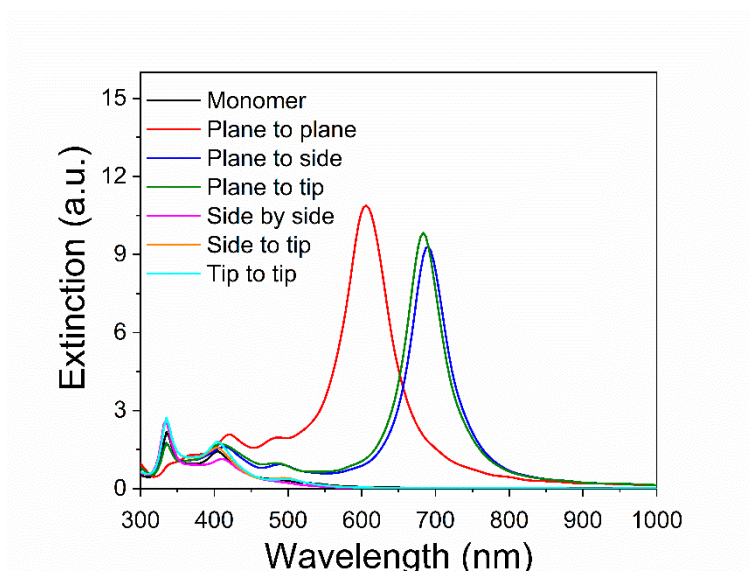


Figure S3. The extinction spectra of the monomer and the six assembly forms of Ag TNPs (the polarization was set perpendicular to the coupling direction).

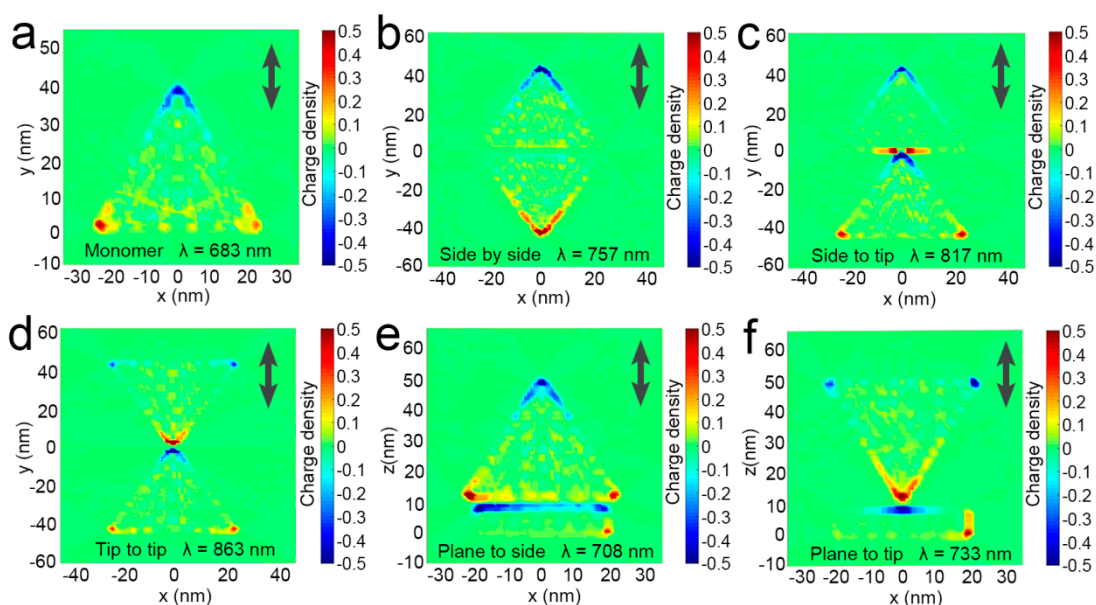


Figure S4. The charge distributions of monomer (a), side-by-side (b), side-to-tip (c), tip-to-tip (d), plane-to-side (e), and plane-to-tip (f) assembly form. The polarization was shown by the arrow in the figures.

All of the samples used for the deposition on the TEM grid are not concentrated or diluted. The Ag TNPs concentration is about $2.59 \times 10^{14}/\text{L}$.

The particle concentration of Ag TNPs was determined by argentometric titrations. In detail, 4 mL of Ag TNPs with the absorption peak at 700 nm was concentrated to 400 μL by centrifuging (10,000 rpm, 10 min). Nitric acid (100 μL , 10 mM) was added to the

concentrated Ag TNPs to dissolve the nanoparticle into silver ion. Then, potassium chromate (12.5 mM) was added until the solution became brick-red, and the volume of the used potassium chromate was recorded.

The particle concentration of Ag TNPs (C_{np}) can be calculated by blow formula:

$$C_{Ag} = 2 * V_{pc} * C_{pc} / V_{np}$$

$$C_{np} = C_{Ag} * WM_{Ag} / (V_t * \rho_{Ag})$$

$$V_t = 0.5 * L_{Ag} * H_{Ag} * T_{Ag}$$

C_{Ag} is the concentration of Ag ions. C_{pc} is the concentration of potassium chromate (12.5 mM). V_{pc} is the volume of used potassium chromate (35 μ L). V_{np} is the volume of Ag TNPs solution (4 mL). WM_{Ag} is the molecular weight of silver (107.8682). ρ_{Ag} is the density of pure silver (10.5 g/mL). V_t is the average volume of single Ag TNP. L_{Ag} is the average edge length of Ag TNPs (50 nm). H_{Ag} is the average height of Ag TNPs. T_{Ag} is the average thickness of Ag TNPs (8 nm).

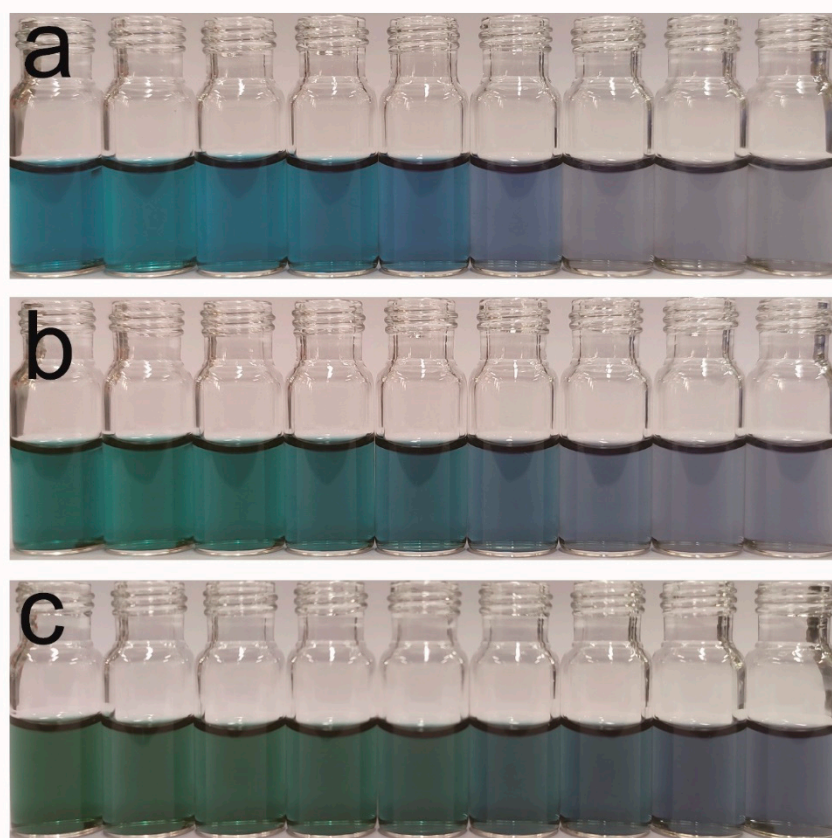


Figure S5. The digital photographs of the Ag TNPs with main absorption peaks at 650 nm (a), 700 nm (b), and 750 nm (c).

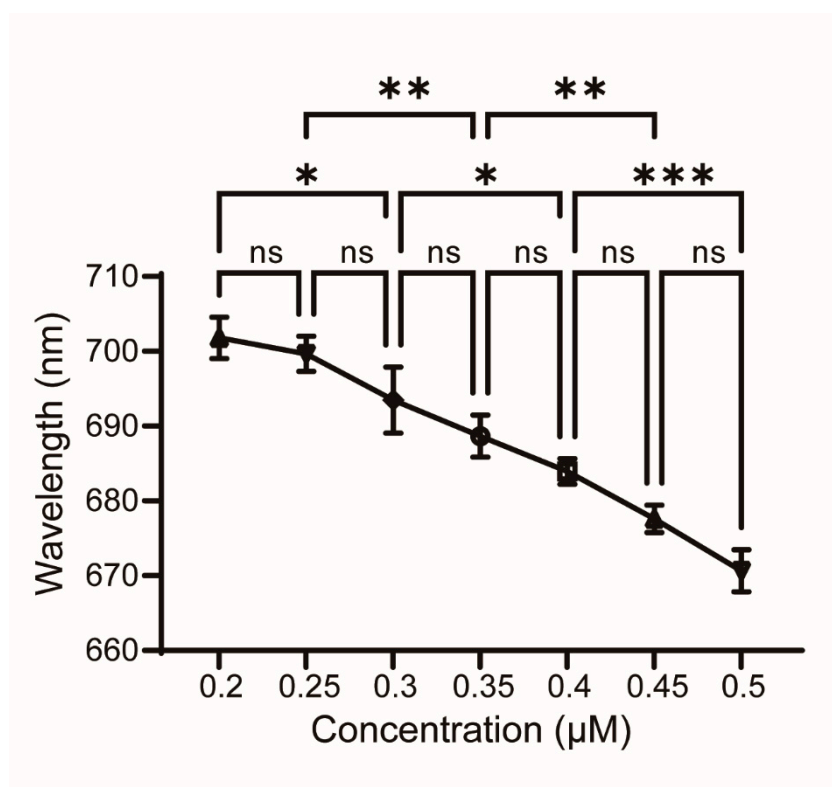


Figure S6. The statistically significant differences analyses of the experimental results. If a p-value is

bigger than 0.05, it is flagged with “ns”. If a p-value is less than 0.05, it is flagged with one star (*). If a p-value is less than 0.01, it is flagged with 2 stars (**). If a p-value is less than 0.001, it is flagged with three stars (***)

Tetraethylthiuram disulfide, a commonly used drug for abstinence, was selected to be detected by the method proposed in this paper. The absorption spectra and the peak positions change trend are shown in Figure S7. Similar to thiram, the main absorption peak gradually blue shifted and the intensity decreased with the concentration of tetraethylthiuram disulfide increasing. These results can not only prove the aggregation mechanism proposed by us but also indicate the potential of our method for the detection of tetraethylthiuram disulfide.

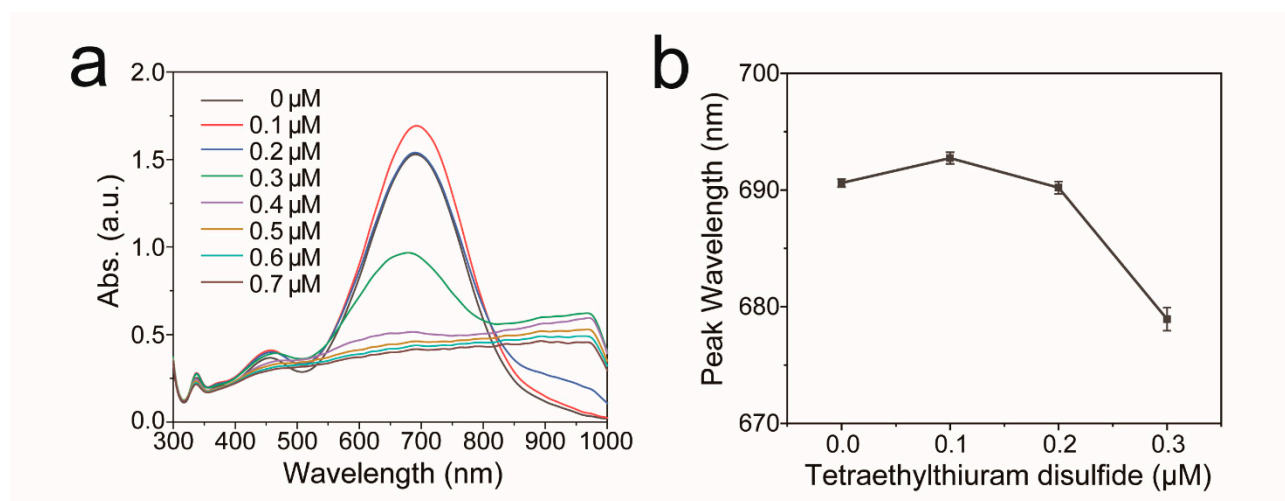


Figure S7. The absorption spectra of the Ag TNPs with main absorption peak at 700 nm after adding different concentrations of tetraethylthiuram disulfide (a). The peak positions change trend with the concentration of tetraethylthiuram disulfide increasing (b).



Figure S8. The digital photographs of the Ag TNPs after adding thiram ($0.6 \mu\text{M}$) and other interfering pesticides ($30 \mu\text{M}$) relative to the sample without any pesticides, respectively.

To evaluate the performance of this method, we compared it with different colorimetric methods for the detection of thiram in the literature, as shown in Table S1. Among them, although the reported method using ligand-free gold nanoparticles has a better LOD and detection range, a preconcentration process is necessary by solid phase extraction [3]. In our method, the detection of thiram can be realized without modification or extraction procedures. So, the detection method proposed in this manuscript is simpler.

Table S1. Performance comparison of different colorimetric methods for the detection of thiram.

Colorimetric methods	LOD	Detection linear range	Quantitative method	Extra modification
Gold nanoparticles [2]	$0.17 \mu\text{M}$	$0.2\text{--}10 \mu\text{M}$	Absorbance	No
Gold nanoparticles [3]	45 nM	$0.1\text{--}0.73 \mu\text{M}$	Absorbance ratio	No
Cyclen dithiocarbamate functionalized silver nanoparticles [4]	$2.81 \mu\text{M}$	$10.0\text{--}20.0 \mu\text{M}$	Absorbance ratio	Yes
Polyvinyl alcohol-decorated Au nanoparticles [5]	19.2 nM	$0.02\text{--}8.32 \mu\text{M}$	Reflectivity value ratio	Yes
Amine-functionalized Ag nanoparticles [6]	$0.036 \mu\text{M}$	$0.1\text{--}100 \mu\text{M}$	Absorbance ratio	Yes
Copper nanoparticles [7]	$0.17 \mu\text{M}$	$0.5\text{--}25 \mu\text{M}$	Absorbance ratio	No
Gold nanoparticles encoded with 4-aminothiophenol [8]	$0.04 \mu\text{M}$	$0.05\text{--}2.0 \mu\text{M}$	Absorbance ratio	Yes
Triangular silver nanoplates (This work)	$0.13 \mu\text{M}$	$0.2\text{--}0.5 \mu\text{M}$	Absorbance	No

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