

Electronic Supplementary Information

Combined Cloud Point Extraction and Tween 20-stabilized Gold Nanoparticles for
Colorimetric Assay of Silver Nanoparticles in Environmental Waters

Zong-Han, Wu and Wei-Lung Tseng*

Department of Chemistry, National Sun Yet-sen University, 70, Lien-hai Road,
Kaohsiung, 804.

Correspondence: Dr. Wei-Lung Tseng, Department of Chemistry, National Sun
Yat-sen University, 70, Lien-hai Road, Kaohsiung, Taiwan 804.

E-mail: tsengwlentangledmail.nsysu.edu.tw

Fax: 011-886-7-3684046.

Experimental Section

Synthesis of the Fe₃O₄ NPs. FeCl₃·6H₂O (2.16 g) and FeCl₂·4H₂O (0.8 g) were dissolved in 20 ml of deionized water. The mixture was deoxygenated by bubbling with nitrogen gas for 10 min and then heated to 80 °C with stirring in a round-bottom flask. Subsequently, aqueous NH₄OH (8M, 10 mL) was added rapidly to the heated solution, which was left to stir for 1 h. After cooling to room temperature, the formed NPs were rinsed four times with deionized water and then resuspended in N₂-saturated water (100 mL). The concentration of Fe₃O₄ NP was estimated to be ~10 mg/mL. TEM images displayed that the diameter of the Fe₃O₄ NPs was 13 ± 1 nm.

Synthesis of the PtNPs. A solution of H₂PtCl₆·(H₂O)₆ (0.2%, 36 mL) was added to boiling deionized water (464 mL) for 1 min. Subsequently, a mixture (11 mL) of 1% sodium citrate and 0.05% citric acid was added to a boiling solution of H₂PtCl₆·(H₂O)₆. After 30 s, a freshly prepared NaBH₄ (0.08%, 5.5 mL) solution containing 1% sodium citrate and 0.05% citric acid was rapidly injected to the resulting solution. After 10 min, a solution of the formed PtNPs was cooled down to room temperature. TEM image show that the diameter of the PtNPs was 5 ± 0.6 nm

Synthesis of the CdSe QDs. We prepared aqueous solution consisting of citrate (0.05 g), Cd(ClO₄)₂ (6 mL, 0.04 M), *N,N*-dimethylselenourea (1.2 mL, 0.01 M), and 45 mL deionized water. The solution was bubbled with nitrogen for 10 min. The resulting mixture was adjusted to pH 9.0 using NaOH (0.1 M, 175 µL) and then they were heated in a conventional 750 W microwave oven (Sharp, Japan) for 120 s. The emission wavelength citrate-capped CdSe QDs is 543 nm. According the previous study, the diameter and concentration of the CdSe QDs was calculated to be 2.8 nm and 1600 nM, respectively.

Synthesis of the CdTe QDs. Sodium borohydride (0.08 g) was reacted with

tellurium powder (0.127 g) in water (1.0 mL) to produce sodium hydrogen telluride (NaHTe, 0.99 M). The NaHTe solution (0.6 mL) was then added to a N₂-saturated mixture (74.8 mL; pH 11.2) of MPA (3.8 mM) and CdClO₄ (16 mM) to give a final Cd²⁺/MPA/HTe⁻ molar ratio of 1:2.4:0.5. The resulting mixture was heated to 96 °C and then subjected to reflux for as long as 1 h to promote the growth of the CdTe QDs. The emission wavelength of MPA-capped CdTe QDs is 612 nm. According the previous study, the diameter and concentration of the CdTe QDs was calculated to be 4.0 nm and 890 nM, respectively.

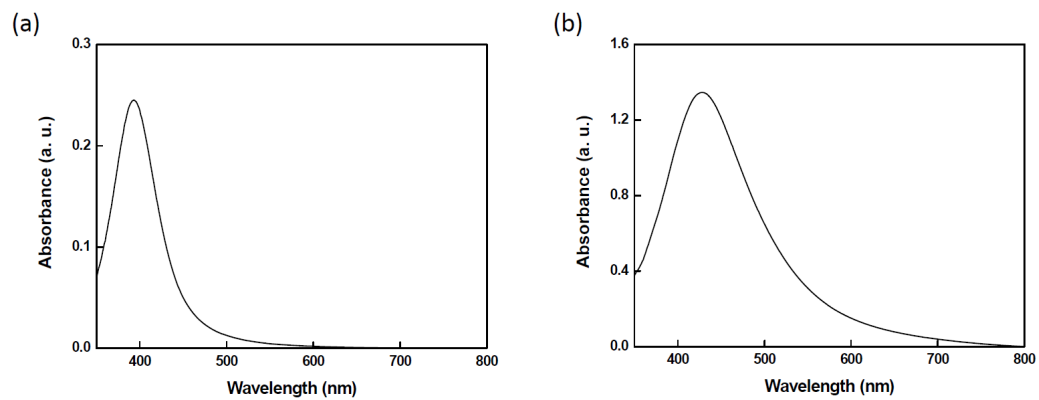


Fig. S1. Extinction spectrum of a solution of 10 and 54 nm AgNPs.

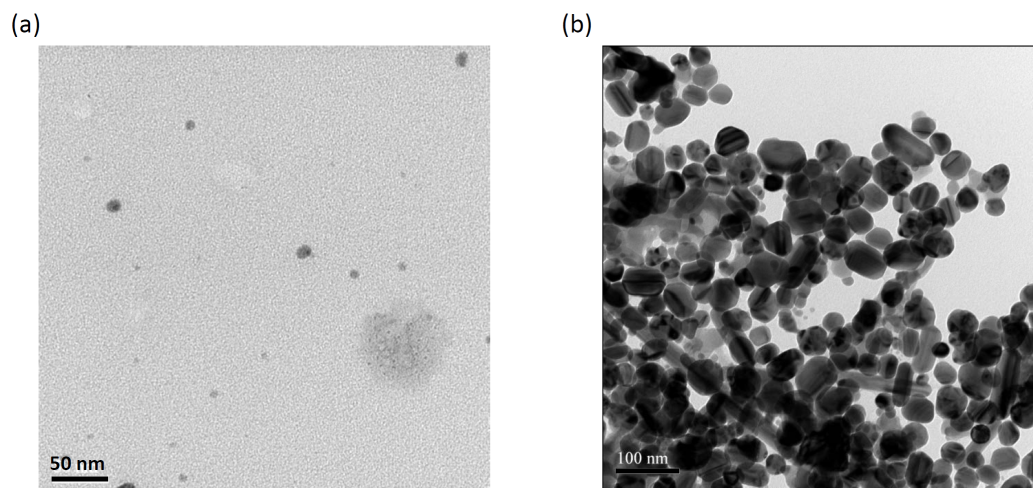


Fig. S2. TEM image of a solution of 10 and 54 nm AgNPs.

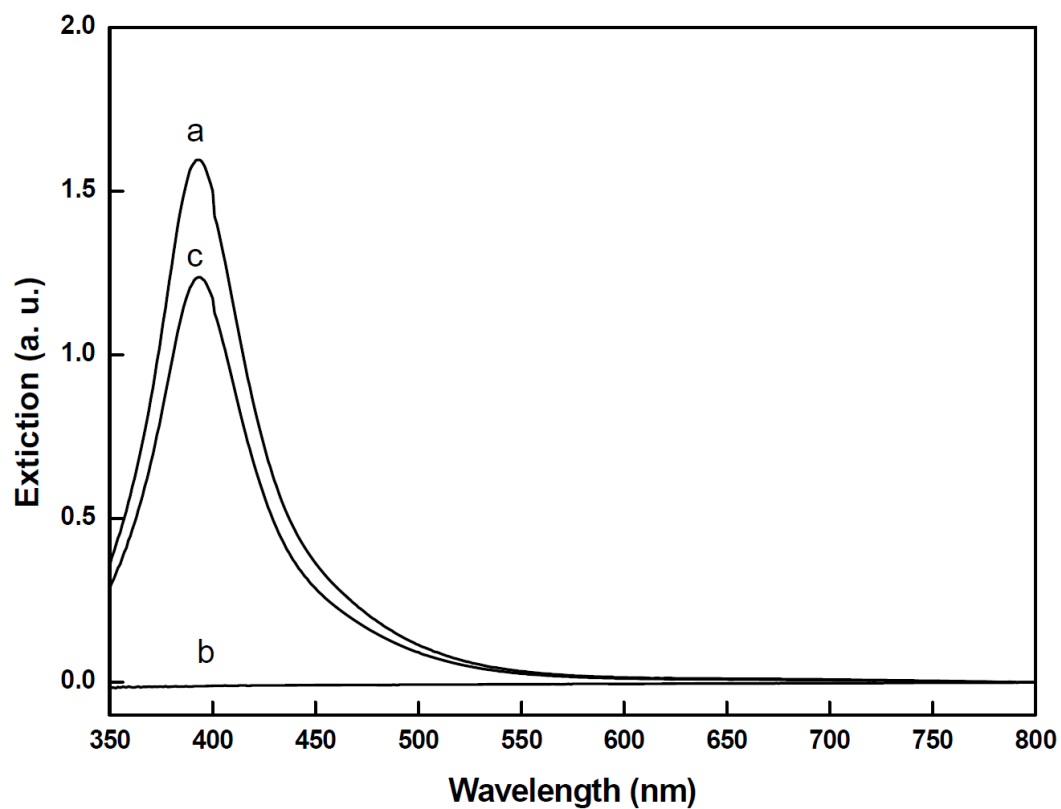


Fig. S3. Extinction spectra of solutions of (a) 10 nm AgNPs and (b, c) the supernatants. (b) A solution of 10 nm AgNPs was extracted with Triton X-114-based CPE. After 30 min, the supernatant was obtained from centrifugation (3900 g, 5 min) of the resulting solution. (c) The supernatant was obtained from centrifugation (65000 g, 90 min) of a solution of 10 nm AgNP.

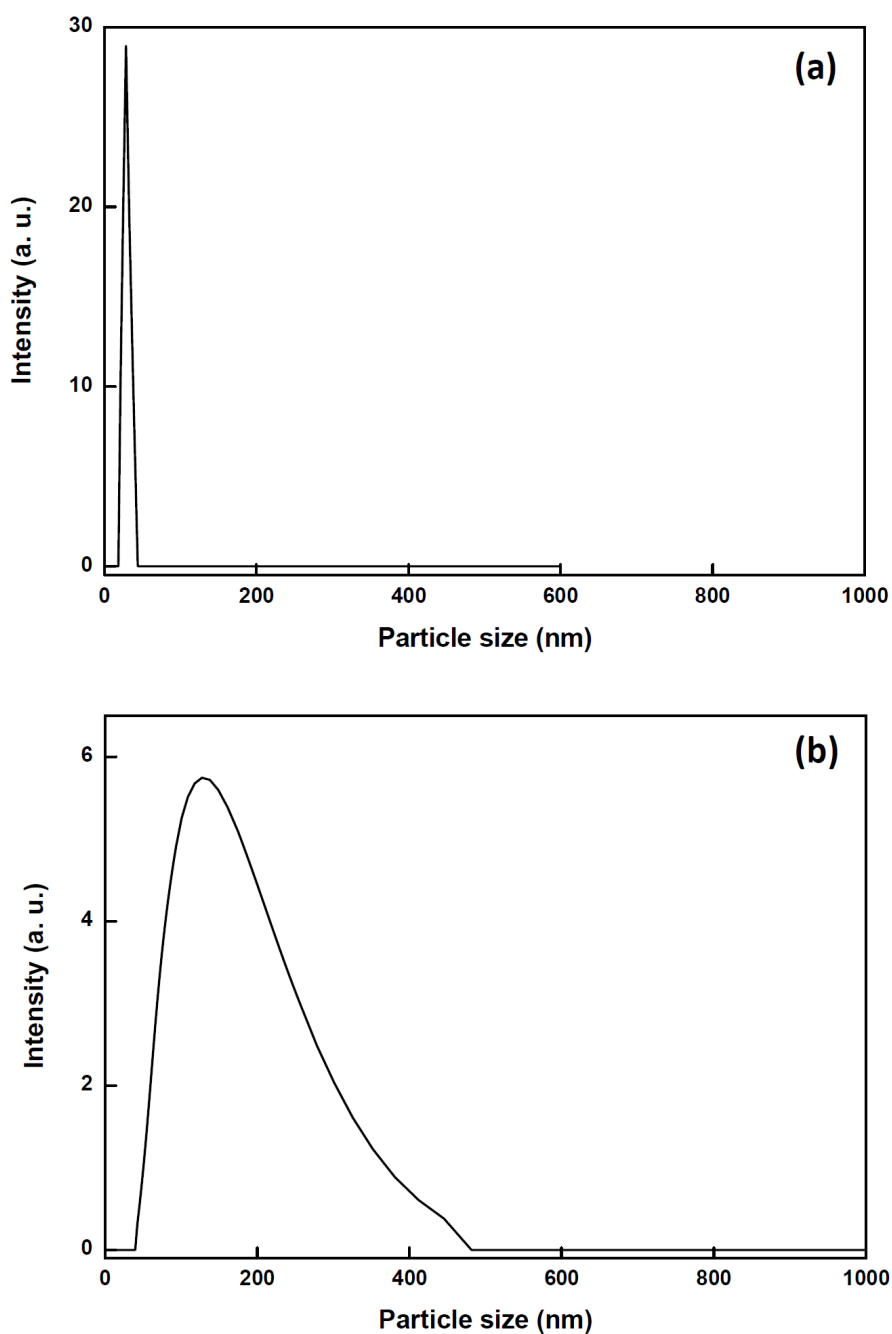


Fig. S4. DLS spectra of solutions of Tween 20-AuNPs (a) before and (b) after the addition of H_2O_2 -oxidized AgNPs. A solution containing 0.01 M $\text{Na}_2\text{S}_2\text{O}_3$ and 0.2% Triton X-114 was used to extract 10 mL of 1.7 $\mu\text{g}/\text{mL}$ AgNPs (10 nm). The extracted AgNPs were oxidized to Ag^+ in a solution of 1 mM H_2O_2 , 1 μM H_3PO_4 , and 20% ethanol for 30 min. The incubation time between H_2O_2 -oxidized AgNPs and Tween 20-AuNPs was 5 min.

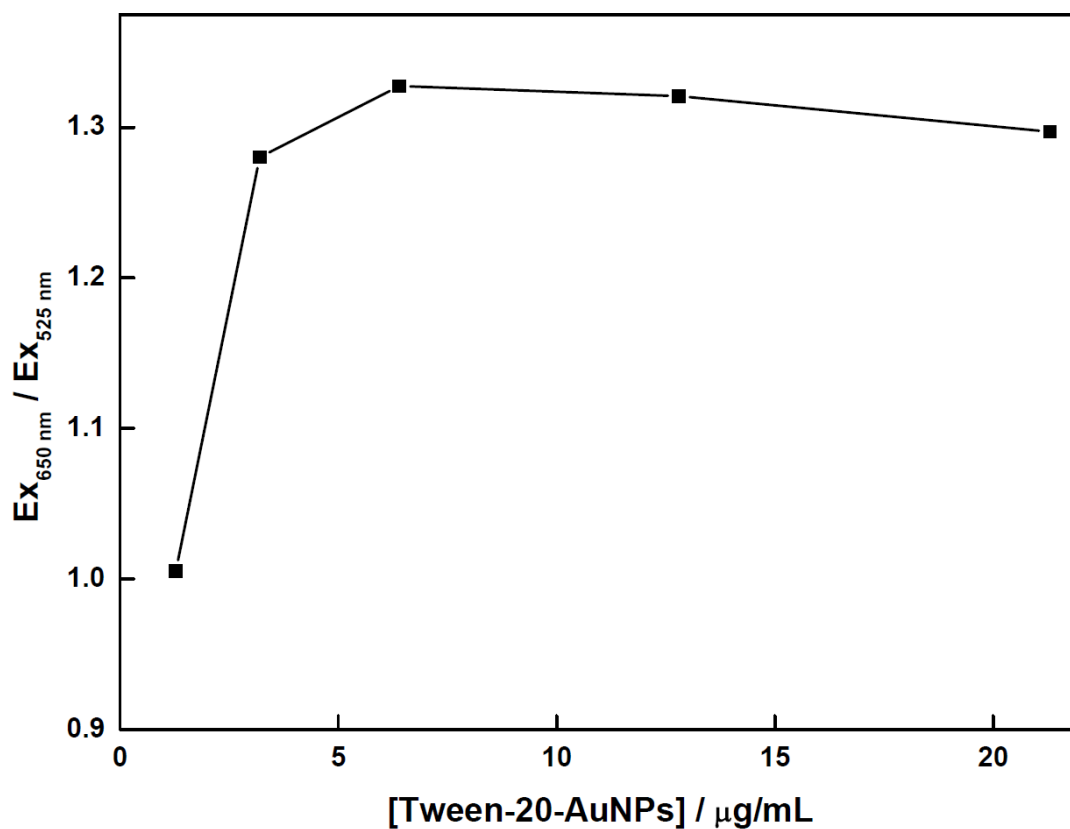


Fig. S5. Effect of the concentration of Tween 20-AuNPs on the detection of H_2O_2 -oxidized AgNPs. A solution containing 0.01 M $\text{Na}_2\text{S}_2\text{O}_3$ and 0.2% Triton X-114 was used to extract 10 mL of 1.7 $\mu\text{g/mL}$ AgNPs (10 nm). The extracted AgNPs were oxidized to Ag^+ in a solution of 1 mM H_2O_2 , 1 μM H_3PO_4 , and 20% ethanol for 30 min.

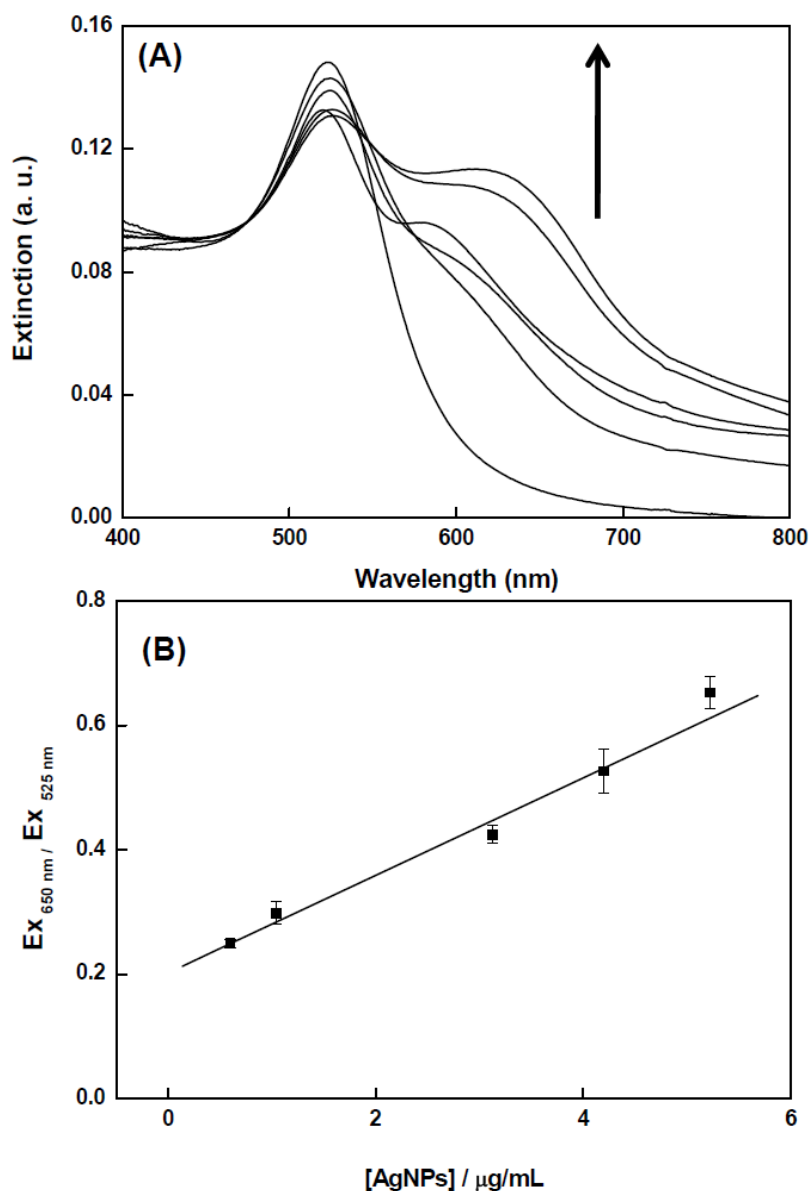


Fig. S6. (A) Extinction spectra change of solutions of 0.26 nM Tween 20-AuNPs upon the addition of different concentrations of H₂O₂-oxidized AgNPs. The arrows indicate the signal changes with increases in analyte concentrations (0, 0.6, 1.0, 3.1, 4.2, and 5.2 μg/mL). A solution containing 0.01 M Na₂S₂O₃ and 0.2% Triton X-114 was used to extract 10 mL of 0.6–5.2 μg/mL AgNPs. The following steps are the same as those in Fig. 3. (B) A plot of the value of EX_{650 nm}/EX_{525 nm} versus the concentration of the AgNPs. The error bars represent standard deviations based on three independent measurements.

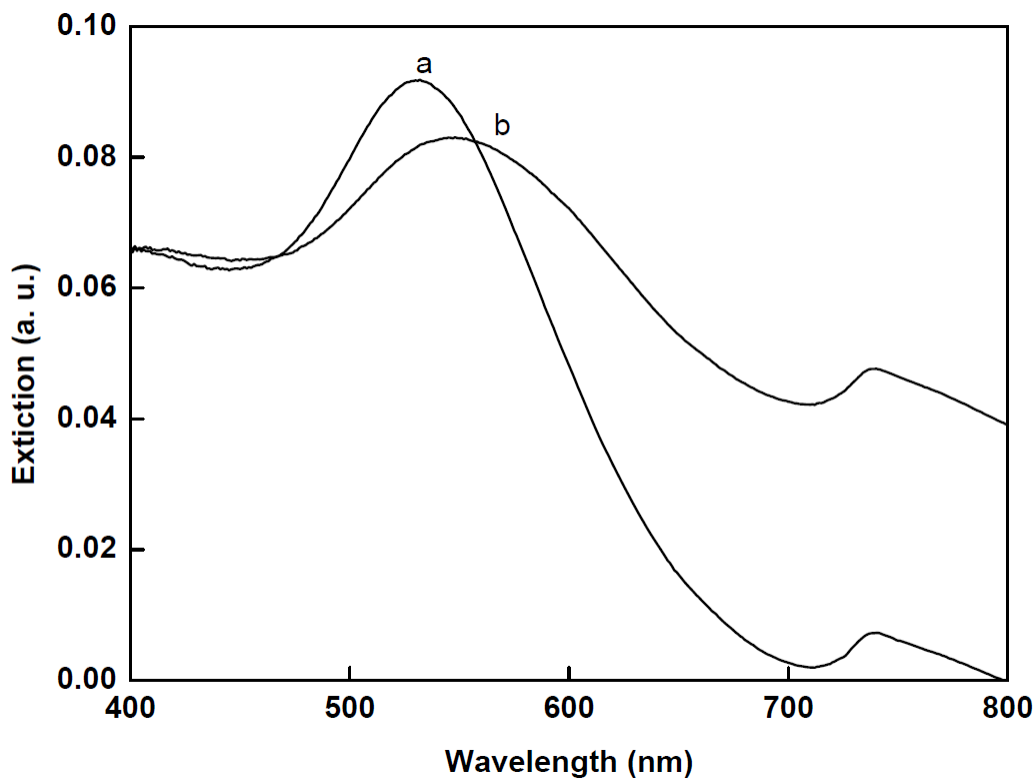


Fig. S7. Extinction spectra of solutions of 0.26 nM Tween 20-AuNPs (a) before and (b) after the addition of H₂O₂-oxidized AgNPs. A solution containing 0.01 M Na₂S₂O₃ and 0.2% Triton X-114 was used to extract 10 mL of AgNPs (850 ng/mL, 7 nm) in artificial water. The extracted AgNPs were oxidized to Ag⁺ in a solution of 1 mM H₂O₂, 1 μM H₃PO₄, and 20% ethanol for 30 min. The incubation time between H₂O₂-oxidized AgNPs and Tween 20-AuNPs was 5 min.

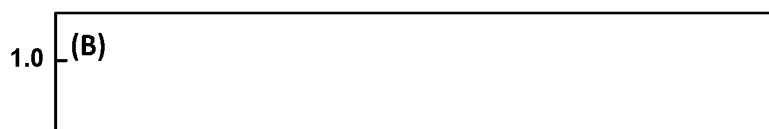
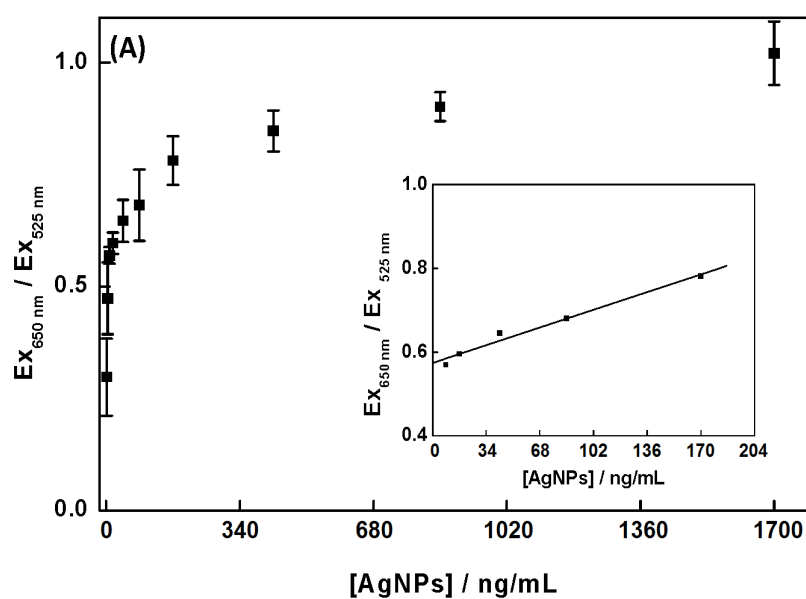


Fig. S8. Colorimetric detection of small-sized AgNPs in (A) tap water and (B) seawater by combining Triton X-114-based CPE and Tween 20-AuNPs. Tap water and seawater samples were spiked by standard solutions containing 1.7–1700 ng/mL AgNPs prior to centrifugation. A solution containing 0.01 M $\text{Na}_2\text{S}_2\text{O}_3$ and 0.2% Triton X-114 was used to extract 10 mL of AgNP-spiked tap water and seawater. The following steps are the same as those in Fig. 4. Inset: Plots of the value of $EX_{650 \text{ nm}}/EX_{525 \text{ nm}}$ versus the concentrations of AgNPs. The error bars represent standard deviations based on three independent measurements.