

# Rapid Chromatographic Separation of Dissoluble Ag(I) and Silver-Containing Nanoparticles of 1-100 Nanometer in Antibacterial Products and Environmental Waters

## Supporting Information

Xiao-Xia Zhou, Rui Liu, and Jing-Fu Liu\*

State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P. O. Box 2871, Beijing 100085, China.

Total figures: 3

\* Corresponding author.

Tel.: +86-10-62849192; Fax: +86-10-62849192;

E-mail: [jfliu@rcees.ac.cn](mailto:jfliu@rcees.ac.cn)

**Preparation and Characterization of GSH-protected Ag Nanoclusters.** The GSH-protected Ag nanoclusters were synthesized following previously reported strategies.<sup>1,2</sup> Briefly, 169 mg of GSH (0.55 mmol) was added into AgNO<sub>3</sub> aqueous solution (25 mL, 5 mM) under vigorous stirring. Then, the mixture was cooled in an ice bath for 30 min. An aqueous solution (6.25 mL) containing 47.5 mg of NaBH<sub>4</sub> (1.25 mmol) was also cooled in ice bath for 30 min. Subsequently, the NaBH<sub>4</sub> solution was added dropwise to the cold GSH-Ag mixture at stirring, and the color immediately turned from white to light yellow. The mixture was allowed to stir for an additional 1 h in ice bath, yielding a deep reddish brown solution. The nanoclusters were precipitated with the addition of 10 mL of methanol. The mixture was centrifuged at 6000 rpm for 10 min. Then, the precipitate obtained was washed with fresh methanol for another 2 times to remove the unreacted reactants. Finally, the precipitate was dried under vacuum for overnight. The Ag nanoclusters were re-dispersed in ultrapure water and ultrafiltrated with Amicon Ultra-15 centrifugal filter units (100 KD, Millipore, MA). Then, the filtrate was collected for use. Identification and characterization of Ag nanoclusters were shown in Figure S3.

**Synthesis and Characterization of AgNPs and Ag<sub>2</sub>S NPs.** Two different coatings stabilized AgNPs (PVP-AgNPs and PVA-AgNPs) were synthesized using the methods reported in the literature.<sup>3,4</sup> The PVP-AgNPs were prepared as follows: (i) dissolving PVP (10 g) in 75 mL of ethylene glycol, into the solution was added 400 mg AgNO<sub>3</sub> under vigorous stirring, kept stirring until AgNO<sub>3</sub> was dissolved completely; (ii) the mixture was heated up to 120 °C at a constant rate of 1 °C/min, and kept at 120 °C for another hour, then the solution was cooled in tap water to room temperature; (iii) to precipitate AgNPs, 300 mL of acetone was introduced into the mixture and followed by centrifugation at 7000 rpm for 25 min, and AgNPs were further washed with ultrapure water using the same procedure for three cycles.

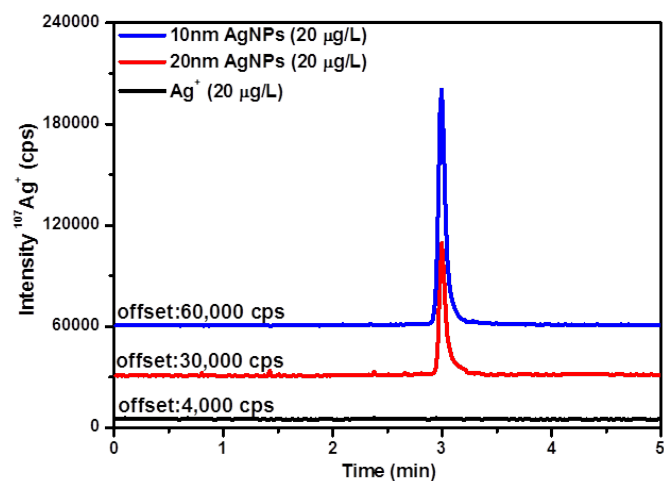
Poly(vinyl alcohol)-124 (PVA) capped AgNPs were synthesized by reduction of AgNO<sub>3</sub> with KBH<sub>4</sub> and stabilized with PVA. Briefly, 0.3 mL of PVA aqueous solution (10%, m/v) was added into 50 mL of KBH<sub>4</sub> solution (20 mM) in an ice bath. Under vigorous stirring, AgNO<sub>3</sub> solution (50 mL, 200 mM) was rapidly injected into the ice-cooled mixture. After several minutes, the resulting solution was centrifuged at 14000 rpm for 10 min and further washed with ultrapure water for three times.

The Ag<sub>2</sub>S NPs were prepared with procedure modified from literature.<sup>5</sup> Briefly, 60 mg bis(p-sulfonatophenyl)phenylphosphane dehydrate dipotassium salt (BSPP) was added into 30 mL of dissolved AgNO<sub>3</sub> aqueous solution (1 mM) to complex with Ag<sup>+</sup>. After stirring for 1 h, 1 mL of Na<sub>2</sub>S aqueous solution (50 mM) was fleetly added into the BSPP-Ag<sup>+</sup> mixture, which accompanied a series of color changes and finally produced a brown Ag<sub>2</sub>S hydrosol.

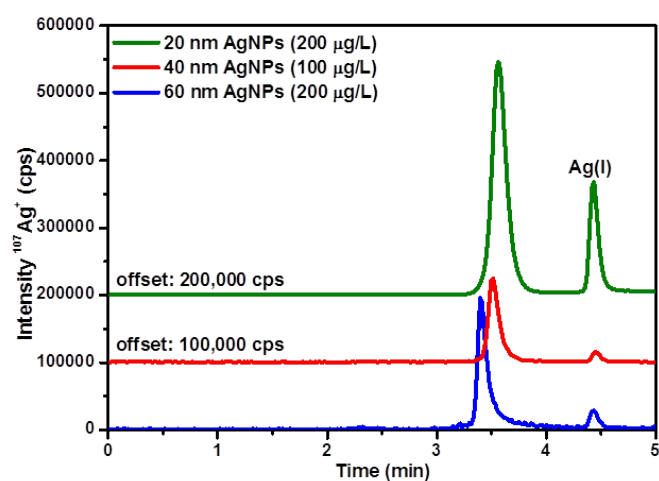
The TEM images and size distribution of the two AgNPs and AgS NPs synthesized above were shown in Figure S3.

## Reference

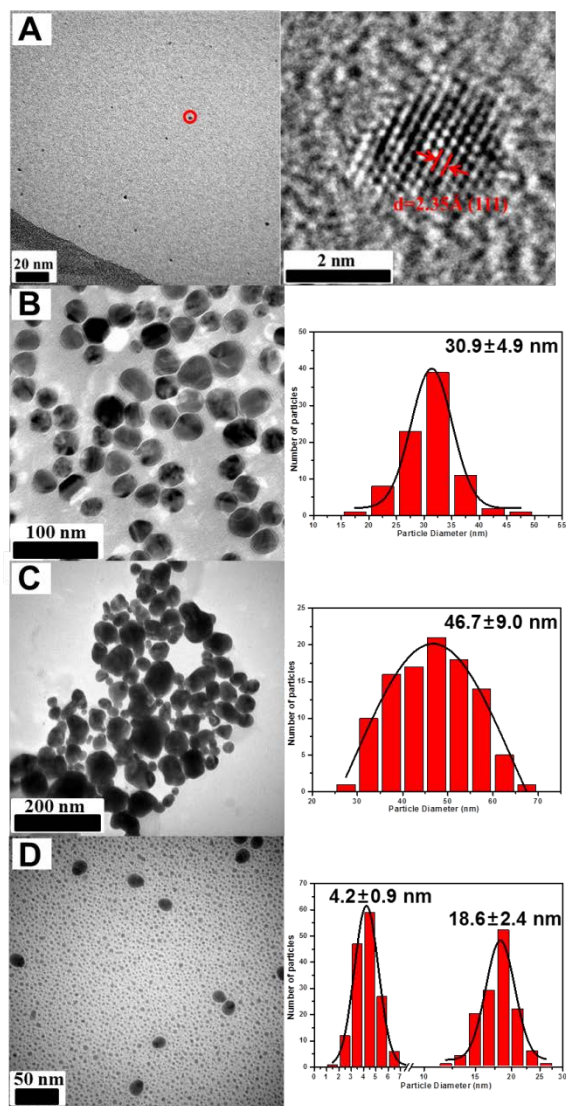
- (1) Pettibone, J. M.; Gigault, J.; Hackley, V. A. Discriminating the states of matter in metallic nanoparticle transformations: What are we missing? *ACS Nano* **2013**, 7 (3), 2491-2499.
- (2) Kumar, S.; Bolan, M. D.; Bigioni, T. P. Glutathione-stabilized magic-number silver cluster compounds. *J. Am. Chem. Soc.* **2010**, 132 (38), 13141-13143.
- (3) Silvert, P. Y.; HerreraUrbina, R.; Duvauchelle, N.; Vijayakrishnan, V.; Elhsissen, K. T. Preparation of colloidal silver dispersions by the polyol process .1. Synthesis and characterization. *J. Mater. Chem.* **1996**, 6 (4), 573-577.
- (4) Chio, O.; Hu, Z. Q. Size dependent and reactive oxygen species related nanosilver toxicity to *Nitrifying bacteria*. *Environ. Sci. Technol.* **2008**, 42 (12), 4583-4588.
- (5) Yang, J.; Ying, J. Y. Nanocomposites of Ag<sub>2</sub>S and noble metals. *Angew.Chem., Int. Ed.* **2011**, 50 (20), 4637-4643.



**Figure S1.** Chromatograms of AgNPs and  $\text{Ag}^+$  under chromatographic conditions: amino column, 500 Å poresize; mobile phase, 0.1% (v/v) FL-70, 0.7 mL/min.



**Figure S2.** Chromatograms of the 20, 40 and 60 nm nominal diameter AgNPs by the proposed method. Chromatographic conditions; amino column, 500 Å poresize; mobile phase, 0.1% (v/v) FL-70 and 2 mM  $\text{Na}_2\text{S}_2\text{O}_3$ , 0.7 mL/min.



**Figure S3.** Identification and characterization of Ag nanoclusters and AgNPs. (A) TEM and HRTEM of Ag nanoclusters; (B) TEM and size distribution of PVP-AgNPs; (C) TEM and size distribution of PVA-AgNPs; (D) TEM and size distribution of Ag<sub>2</sub>S NPs.