Preparation and Structure of Water-dispersible Silver Nanoparticles with Highly Positively Charged Surface

Tetsu Yonezawa, *** Hideo Genda, * Tetsuya Itoh, * and Kunihito Koumoto * *Department of Applied Chemistry, Graduate School of Engineering, Nagoya University Furo-cho, Chiuksa, Nagoya 464-8603, Japan **Department of Chemistry, School of Science, The University of Tokyo 7-3-1, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan Fax: 81-3-5841-2356, e-mail: yonezawa@chem.s.u-tokyo.ac.jp

Silver nanoparticles with highly positively charged surface were successfully and reproducibly prepared by NaBH₄ reduction of Ag ions in the presence of a small cationic sulfur ligand. Insoluble silver chloride was chosen as the silver sauce. The obtained particles were spherical and highly uniform and readily dispersed into aqueous media. Preparative conditions were examined.

Key words: Silver, Nanoparticle, Cationic, Assembly, Hydrosol

1. INTRODUCTION

Since the pioneering report by Brust et al.,[1,2] many kinds of thiol-stabilized nanoparticles have been prepared and detailed structural analyses have been carried out. Especially, such thiol-stabilized metal nanoparticles can be readily purified and used as functional units in the field of chemistry, physics, biology, materials science, and surface science.[3-5] Various thiols have been prepared for nanoparticle stabilization. Ionic thiols were often used to obtain nanoparticle hydrosols, and such nanoparticles can be used as the units for template-mediated nanoparticle assemblies which are generated by electrostatic interactions between nanoparticles and templates.

Among many studies, we propose the use of quaternary ammonium terminated thiols or disulfides as the stabilizer molecules.[6-8] As quaternary ammonium groups can be ionized in aqueous media at any pH, the particle surface is always positively charged.[6] When such a ligand with a relatively long alkyl chain was used as the stabilizing reagent of gold nanoparticles, the particles could be dispersed into aqueous media under severe acid and alkaline conditions.[6] We have also introduced isocyanide type quaternary ammonium ligands for nanoparticles of palladium.[9] Such nanoparticles with a positively charged surface should be very useful for preparation of a low-dimensional assembly with a suitable template.[10-12] We have reported that cationic gold nanoparticles can be one-dimensionally aligned by using DNA, which can work as a rigid anionic 1D polymer template.[10,11] Quite recently, Warner published similar results.[13] Especially, by using thiocholine bromide (TCBr)staibilized gold nanoparticles, they automatically fused on DNA molecules to form nano-wire like structures even at room temperature.[11]

In this manuscript, we would like to describe preparation and structure of cationic silver nanoparticles which are stabilized by TCBr.[8] The preparative procedure will be discussed in detail.



Fig. 1 Preparative procedure of silver nanoparticles with positively charged surface.

2. EXPERIMENTAL

Water was purified by a Mili-Q system (>18 M Ω). As the stabilizing reagent, thiocholine bromide (TCBr, HS-(CH₂)₂-N(CH₃)₃⁺ Br) was selected. TCBr was synthesized by hydrolysis of acetylthiocholine bromide (Aldrich or ACROS) by HBr. The purity of this product was confirmed by ¹H NMR, FT-IR and elemental analysis.

Silver nanoparticles studied here were prepared by NaBH₄-reduction of AgCl (Fig. 1). AgCl (6.0×10^{-6} mol dm⁻³) was injected into methanol or water containing TCBr (30 cm^3 , 6.0×10^{-6} mol dm⁻³) in an as-received colorless powder form. Under vigorous stirring, an aqueous solution of NaBH₄ (5cm^3 , 4.0×10^{-1} mol dm⁻³) was injected dropwise with a syringe pump (injection speed: 1 cm³/min) at room temperature. The obtained nanoparticles were purified by the re-precipitation.

3. RESULTS AND DISCUSSION

In this study, water-dispersible silver nanoparticles were prepared from an insoluble silver salt: AgCl. At first stage, the solution was colorless and AgCl powder was stirred in the flask. But after the addition of the reducing reagent: NaBH₄, the color of the dispersion changed into yellow-brown. This color change strongly supported the formation of nanosized Ag particles, not



Fig. 2 Transmission electron micrographs of TCBr-stabilized silver nanoparticles prepared (a) in methanol and (b) in water. The metal source is AgCl.

Table I. Average diameter and relative standard deviation of TCBr-stabilized Ag nanoparticles

Disperse medium	Average diameter / nm	Relative SD* / %
methanol	5.9	6.8
water	9.0	6.6

*relative standard deviation

in a large bulk state. The obtained dispersions in the both media (methanol and water) were clear and stable, and no precipitate was observed in the flasks. We have also prepared Ag nanoparticles from water-soluble AgNO₃. Comparing the two metal sources, slower color change was observed in the case of AgCl. As our stabilizing reagent was TCBr, Ag⁺ ions generated from AgNO₃ in water must be also transferred to insoluble AgBr. However, as no precipitate was observed in that case, generated AgBr should be considerably smaller. Therefore, probably, the supply rate of Ag⁺ ion controls the speed of the formation of Ag nanoparticles. It should be one of the common conventional wisdoms that homogeneous and uniform colloidal solutions should be obtained from homogeneous precursor solutions. In many cases, it might be true. However, in this case, even the metal sources did not dissolve into the solution of stabilizer molecules, homogeneous dispersions of uniform-sized nanoparticles could be obtained.

In Figure 2, transmission electron micrographs of TCBr-stabilized Ag nanoparticles in methanol and water are collected. The both nanoparticles are highly spherical. Small aggregated structures found in these images should be generated with the evaporation of the disperse media during the preparation of the TEM samples from dispersions. TEM samples were prepared by simple dropping of a small amount of dispersions onto carbon-coated copper grids and dried under vacuum. X-ray diffraction measurement revealed that the particles were consisted of metallic silver and no

silver halides were observed.[8] Even from insoluble source, the reduction was completed.

In Table 1, the average particle diameters and the relative standard deviations (standard deviation / average particle diameter) of these nanoparticles prepared in the two solvents are collected. The sizes of more than 100 particles were measured for this purpose. The particle size of Ag nanoparticles prepared in water was considerably larger that prepared in methanol. But the relative standard deviations of the both nanoparticles are as small as 7 %. In the both media, highly uniform nanoparticles were obtained.

The difference of the particle size in the two different disperse media can be attributed to the electrostatic repulsion between TCBr molecules each other, which control the aggregation of silver atoms. In water, quaternary ammonium groups of TCBr molecules are positively ionized and these groups have strong repulsion force each other. However, the length of alkyl chain of TCBr is quite short, (CH₂)₂, the hydrophobic interaction between alkyl groups cannot compensate such strong repulsion. But as Br ions are not perfectly ionized in methanol, the repulsion force between TCBr molecules in methanol should be smaller. Therefore, the rate of stabilization should be faster in methanol than in water. The particle size of metal nanoparticles prepared by such a wet process is determined by the competition between aggregation of 0-valent metal atoms and stabilization of the particle surface by organic stabilizer molecules. TCBr in methanol stabilizes the silver nanoparticles faster than in water. In fact, TCBrstabilized gold nanoparticles could not be reproducibly obtained in water from AuCl₄ but can be obtained in methanol.

4. CONCLUSION

Stable and homogeneous water and methanol dispersions of silver nanoparticles with a highly positively charged surface were obtained by $NaBH_4$ reduction of AgCl. The obtained nanoparticles were extremely spherical and their sizes were highly uniform. Due to the small cationic stabilizer molecule, TCBr, attached to the nanoparticle surface, their sizes were varied with the disperse media.

Acknowledgments

Authors thank Dr. S. Onoue (Kyoritsu Chemical & Co. Ltd.) for his experimental assistance and discussion. This work is partly supported by the Japan Space Utilization Promotion Center (JSUP).

REFERENCES

- M. Brust, M. Walker, D. Bethell, D. J. Schffrin, and R. Whyman, J. Chem. Soc., Chem. Commun., 1994, 801.
- [2] M. Brust, J. Fink, D. Bethell, D. J. Schiffrin, and C. J. Kiely, J. Chem. Soc., Chem. Commun., 1995, 1655.
- [3] T. Yonezawa, S. Onoue, and N. Kimizuka, Adv. Mater., 13, 140 (2001). T. Yonezawa, H. Matsune, and N. Kimizuka, Adv. Mater., 15, 499 (2003).
- [4] N. Toshima and T. Yonezawa, New J. Chem., 1998, 1179. J. S. Bradley, in "Clusters and Colloids", Ed. by G. Schmid, Wiley-VCH, Weinheim (1994) pp. 459-544.

- [5] K. Kimura, S. Sato, and H. Yao, *Chem. Lett.*, 2001, 372. S. Chen and K. Kimura, *Langmuir*, 15, 1075 (1999).
- [6] T. Yonezawa, S. Onoue, and K. Kunitake, *Chem. Lett.*, **1999**, 1061.
- [7] T. Yonezawa, S. Onoue, and N. Kimizuka, *Langmuir*, 16, 5218 (2000).
- [8] T. Yonezawa, H. Genda, and K. Koumoto, Chem. Lett., 32, 194 (2003).
- [9] T. Yonezawa, K. Imamura, and N. Kimizuka, *Langmuir*, 17, 4701 (2001).
- [10] T. Yonezawa, S. Onoue, and T. Kunitake, Koubunshi Ronbunshu, 56, 855 (1999).
- [11] T. Yonezawa, S. Onoue, and N. Kimizuka, *Chem. Lett.*, 2002, 1172.
- [12] T. Yonezawa, S. Onoue, and N. Kimizuka, *Chem. Lett.*, 2002, 528.
- [13] M. G. Warner and J. E. Hutchison, Nature Mater., 2, 272 (2003).

(Received October 23, 2003; Accepted November 17, 2003)