The Characterization of Borohydride-Stabilized Nanosilvers in Laponite Sol Using ¹H NMR: Its Ligand Exchange Reactions with MUA and TOP

Jae-Seok Seo, Dong-Min Son, Hanna Lee, Jeekwang Kim, and Youhyuk Kim[*]

Department of Chemistry and Institute of Basic Sciences, College of Advanced Sciences, Dankook University, Cheonan, Chungnam 330-714, Korea. *E-mail: hyukim@dankook.ac.kr
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In borohydride-protected nanosilvers in laponite sol, the silver particles aggregate to form short chains and a dumbbell shape. The ¹H NMR measurements in this study represent, to our knowledge, the first observation of proton resonances of borohydride-protected nanosilvers in aqueous solution. Borohydride on nanosilver can be exchanged with 11-mercaptoundecanoic acid (MUA) or trioctylphosphine (TOP). Transmission electron microscopy and UV-Vis spectroscopy data show that the number of aggregated silver nanoparticles decreases upon addition of aforementioned ligands due to the formation of silver MPCs (monolayer-protected clusters). Adsorption of MUA or TOP on nanosilver is confirmed through the observation of broad proton resonances of MPCs in ¹H NMR spectra.

Key Words: Borohydride-protected nanosilvers, Laponite, MPCs, 11-Mercaptoundecanoic acid (MUA), ¹H NMR

Introduction

Colloidal nanometals with controllable morphology and size have been widely investigated due to their unique electronic and spectroscopic properties, and their potential applications in electronics, catalysis and optics.[1-10] Reduction of metal ions is most commonly employed in the preparation of metal nanoparticles in aqueous solution. Sodium borohydride has been the choice of reducing agents for Au and Ag nanoparticles because of the advantage in its reducing power over other reducing agents such as hydrazine and ascorbic acid, which give larger nanoparticles.[11,12] A detailed mechanism study of the silver-borohydride system shows that BH_4^- functions not only as a reducing reagent but also as a stabilizing ion to prevent silver sols from aggregation.[13-15] However, the borohydride adsorbed on silver sol is finally consumed by reaction with water, driving the silver sol to aggregate in a catastrophic manner. Because of this behavior, controlling the shape and size of nanoparticles is problematic.

To develop effective preparation methods of nanoparticles with well-controlled shapes and sizes, surfactants or protective colloids have been used to prevent the growth and aggregation of nanoparticles.[16-20] In particular, high concentrations of silver colloidal sol have been obtained by using laponite as a steric barrier to prevent aggregation of silver sol.[21] Laponite is a synthetic polycrystalline similar in structure and composition to natural hectorite, of the smectic group.[22] The empirical composition of laponite is $Na_{0.7}[(Si_8Mg_{5.5}Li_{0.3})O_{20}(OH)_4]$. Nanoparticles in laponite sol would be suitable for biomolecule reactions and biological applications including biosensors and biolabeling because of their water solubility. Although alkanethiols have been used extensively for nanometals as a capping ligand, water-insoluble alkanethiolate monolayers would limit their biological sensing applications.[23] In this paper, we report very stable borohydride-protected nanosilvers in laponite sol and ligand exchange reactions of borohydride-adsorbed silver

sol with 11-mercaptoundecanoic acid (MUA), and trioctylphosphine (TOP).

Experimental

Materials. Analytically pure $AgNO_3$ and $NaBH_4$ (Aldrich, 98%) and redistilled deionized water were used for all sample preparations. Laponite RDS (Rockwood), which contains 10% sodium phosphate, $Na_4P_2O_7$, was used without further purification and was considered as an anionic material with a negative charge (cationic exchange capacity) of about 50 mmol/100 g. MUA (Aldrich, 95%) and trioctylphosphine (Aldrich, 90%) were used as received without further purification.

Synthesis and cryogel production of the borohydride-protected nanosilver in laponite. The borohydride-protected silver colloids in laponite were prepared according to a previously-published procedure.[21] Laponite RDS (4.60 g, 2.30 mmol of negative charge) in 500 mL distilled water was vigorously stirred for half an hour. When the laponite solution turned transparent, excess $NaBH_4$ (0.444 g, 11.5 mmol) was added into laponite solution and stirred for five more minutes. Separately, analytically pure $AgNO_3$ (0.390 g, 2.30 mmol) in 500 mL distilled water was prepared, and silver colloids in laponite sol were generated by slowly adding aqueous silver nitrate solution dropwise into laponite solution containing $NaBH_4$. The final color of the solution was nut brown and consistent with that of stage 3 in ref. 13. A cryogel of the nanosilvers was obtained by using a freeze-drying process using a Samwon deep freezer (SFDS-M24L). These cryogels were used in the ¹H NMR experiment on the borohydride-protected nanosilver.

Synthesis and cryogel production of the silver MPCs (monolayer-protected clusters) from MUA and trioctylphosphine. The MPCs of silver colloids were prepared by the addition of an excess amount of ligands in toluene into the borohydride-protected silver colloid. This solution were transferred into a separation funnel, and the funnel was shaken for 10 minutes.

The resulting microemulsion was allowed to settle for an hour, after which phase separation was complete. The water layer containing the MPC product was collected and freeze-dried to give cryogel powders. The ^{1}H NMR characterization of silver MPCs was done on these powders.

Instrumentation. The absorption spectra of nanosilver in laponite sol were recorded on a UV2201 Shimadzu UV-Vis spectrophotometer using optical quartz cells. Transmission electron microscopic (TEM) micrographs for silver nanoparticles were acquired with JEOL-JEM-3010 operating at 300 kV. ^{1}H NMR spectra in D$_2$O were recorded using a Varian (Unity Inova) 600-MHz spectrometer.

Results and Discussion

General characteristics of aged borohydride-protected nanosilver in laponite. The UV-Vis spectrum of silver nanoparticles in laponite sol shows two absorption bands at 390 nm and at around 560 nm (Figure 1(a)). The absorption band at 390 nm is identical to the surface plasmon band of nanosilver hydrosol.[14] The band near 560 nm is related to the aggregation of nanosilver particles. It is known that the surface plasmon band of noble metal nanoparticles is sensitive to size, shape, surface properties, and surrounding environments.[24,25] For example,
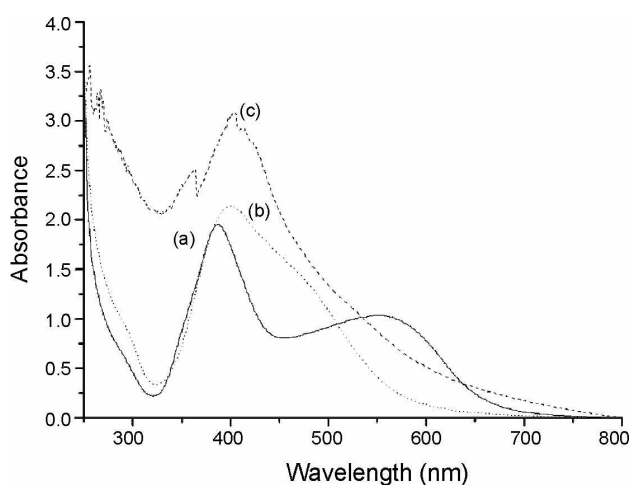

Figure 1. UV-Vis absorption spectra of nanosilvers in laponite sol. protected by (a) borohydride, (b) MUA, (c) trioctylphosphine.

gold nanorods show two absorption bands, one at a shorter wavelength of 525 nm, and the other at a longer wavelength of 740 nm, corresponding to the transverse and longitudinal mode, respectively.[26] Similarly, CTAB (cetyltrimethylammonium bromide)-stabilized nanosilver, which is aggregated with two silver particles, exhibits one narrow absorption band near 408 nm and the other absorbance band at 560 nm.[27] Based on previously-reported results, the band at 569 nm in the UV-Vis spectrum of nanosilver can be assigned to the surface plasmon resonance coupling band of linear-aggregated nanosilver particles. The TEM result is consistent with this assignment, showing that the silver particles aggregate by forming short chains, or in a dumbbell shape. The size of nanosilvers is less than 20 nm (Figure 2(a)). The nanosilver in the laponite sol can be suspended for more than a year without precipitation occurring.

Synthesis and general characteristics of silver MPCs. The ligand exchange reaction between borohydride-protected nanosilver in laponite sol and MUA and TOP was investigated. Typically, varying amounts of ligands were added to borohydride-protected nanosilver in laponite sol and stirred for 1 hour.

Properties of silver MPCs. UV-Vis spectroscopy and transmission electron microscopy (TEM). The UV-Vis spectrum of silver MPCs synthesized from MUA in laponite sol shows a surface plasmon band at 401 nm, indicating a red shift as the surface of nanosilver is modified with MUA (Fig. 1(b)). This shift of the surface plasmon band from 390 nm by capping of silver particles can be attributed to bond formation between nanosilver and the ligands. For example, the surface plasmon band of the nanosilver capped by MUA in CTAB and 1-nonanethiol appears at 400 and 436 nm, respectively, which suggest a bond formation of the S ions and the silver atoms of the nanoparticle.[27,28] The broad band at 475 nm and relatively asymmetrical features suggest that the particle size distribution is not monodispersed. Interestingly, the band at 560 nm which appeared in the borohydride-protected nanosilver disappeared. The TEM image in Figure 2(b) shows that the number of aggregated nanosilvers decreases significantly, suggesting that the formation of silver MPCs plays an important role. This phenomena is more pronounced when trioctylphosphine is exchanged with borohydride on nanosilver in laponite sol. Figure 1(c) shows absorption spectra of trioctylphosphine-protected nanosilver in laponite sol. The absorption bands at 403 and 415 nm
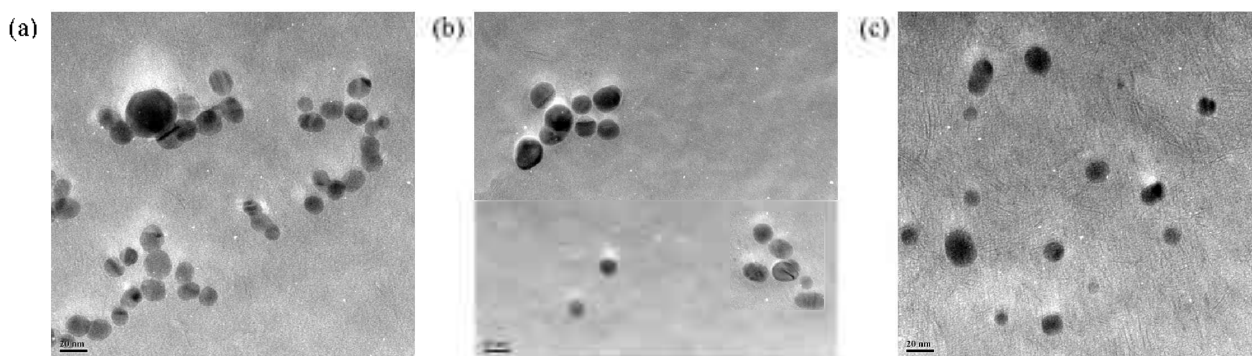

Figure 2. High-resolution transmission electron micrograph of nanosilvers in laponite sol. protected by (a) borohydride, (b) MUA, (c) trioctylphosphine.
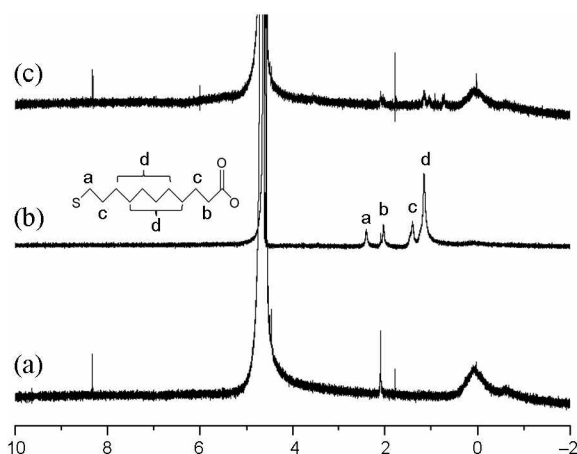
Figure 3. ¹H NMR spectra (D₂O) of nanosilvers in laponite sol, protected by (a) borohydride, (b) MUA, (c) trioctylphosphine.

are assigned as surface plasmon bands of trioctylphosphine-capped nanosilvers due to small and large nanosilvers, respectively. The band at 365 nm might be associated with a coordination compound of silver phosphine. The presence of this band indicates some oxidation of nanosilver during the ligand exchange reaction. The TEM result is consistent with the UV data, as shown in Figure 2(c). The TEM image again shows that the number of aggregated silver nanoparticles is sharply decreased. Although it is not easy to provide a detailed formation mechanism of silver MPCs, ligand exchange with MUA and TOP and consequent redispersion of nanosilvers is likely, since the nanosilvers desorb from the laponite edges, which contain positive charges by losing electrostatic interactions between positively charged edges and BH_4^-. The formation of the mercaptoacetic acid-protected nanosilver shows similar behavior over time: initially-formed aggregated nanosilver gradually changes into spherical particles.[16]

¹H NMR spectroscopy. To determine that borohydride and ligands are bound to the silver core in laponite sol, we obtained ¹H NMR spectra. As expected, signals for nuclei close to the silver core are broadened into the base line.[29-31] The ¹H NMR spectrum of the borohydride-protected nanosilvers shows a very broad resonance from 0.4 to -0.4 ppm, and an additional broad resonance at -0.6 ppm with an integration ratio of 7 to 1 (Figure 3(a)). The protons of NaBH₄ in D₂O are observed as a multiplet from 0.4 to -0.8 ppm (not shown here). The integration ratio of two resonances of the borohydride-protected nanosilver in laponite sol precludes the possibility of bridging hydride which show a resonance at -13.4 ppm for ruthenium borohydride.[32] The resonance at -0.6 ppm seems to be due to different sites on the surfaces of nanosilvers. To our knowledge, this is the first ¹H NMR spectrum of borohydride adsorbed on nanoparticles. The ¹H NMR spectrum of MUA-protected nanosilver in laponite sol showed broad resonances corresponding to the adsorbed ligand, showing that MUA successfully replaced some of the borohydride on the surface of the nanosilver. There were no peaks corresponding to free MUA, which would occur as sharp resonances. The chemical shift of all protons of MUA adsorbed on nanosilver was shifted

upfield relative to their positions in free MUA. The assignment of protons of MUA adsorbed on nanosilver is given in Figure 3(b). The proton resonances at 1.2, 2.0 and 2.4 ppm is assigned as protons of -(CH₂)₆-, -CH₂- next to carboxylate and -CH₂-next to thiol, respectively. Similar chemical shifts have been observed in a mixed MUA and 6-mercapto-1-hexanol protected-nanosilvers in polyvinylpyrrolidone (PVP).[33] The overlap of proton resonances (labeled as c in Figure 3(b)) for -SH, -CH₂-CH₂-SH, -CH₂-CH₂-COO⁻ at 1.4 ppm with integration of 4.3 H makes it hard to assign the thiol proton. Although the thiol-noble-metal bond is most commonly described as a covalent surface-bound thiolate, the thiol-gold system in which intact thiols adsorbed on nanogold have been reported for the dodecanthiol adsorbed on the surface of nanogold.[34] The monolayers of BH_4^- adsorbed on nanosilver can be partially removed by trioctylphosphine. Figure 3(c) shows the ¹H NMR spectrum in D₂O of the trioctylphosphine-protected nanosilver in laponite sol. These results show the same broadening effect, as do monolayers of MUA-protected nanosilvers. There were also no peaks corresponding to free trioctylphosphine, which would occur as sharp resonances. The exact assignment of proton resonances was impossible due to the low intensities of these protons. There was a large portion of borohydride adsorbed on nanosilver in spite of the excess trioctylphosphine used (the mole ratio of trioctylphosphine over Ag⁻ is 5). The incompletion of the exchange reaction seems to be due to the insolubility of free trioctylphosphine in water.

Conclusions

Borohydride-protected nanosilver in laponite sol is remarkably stable. It can be suspended for more than a year without precipitation occurring. A plausible explanation is the blocking effect of laponite functioning as a steric barrier for collision between borohydride adsorbed on nanosilver. Similar effects have been reported, that the reaction rate of nanosilver oxidation with O₂ was greatly inhibited when the nanoparticles were stabilized with CTAB.[35] An interesting feature of the exchange reaction described herein is that the number of aggregated silver nanoparticles was significantly decreased. The borohydride-protected nanosilver in laponite sol may have advantages that one can control the variations in the shapes of the silver particles with appropriate ligands.

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