Preparation and Stabilization of Ag Nanoparticles in 1-Amino-4-methylpiperazine

Heon-Soo Park,[†,‡] Ueon Sang Shin,[†,‡] Hae-Won Kim,[†,‡,§] and Myoung-Seon Gong[†,‡,*]

[†]*Department of Nanobiomedical Science & WCU Research Center, Dankook University Graduate School, Korea*
[*]*E-mail: msgong@dankook.ac.kr*
[‡]*Institute of Tissue Regeneration Engineering (ITREN), Dankook University, Korea*
[§]*Department of Biomaterials Science, School of Dentistry, Dankook University, Korea*

Uniform Ag nanoparticles (< 10 nm) were effectively prepared in 1-amino-4-methylpiperazine as a solvent with multiple functions including reduction and stabilization. An Ag-complex such as $Ag_2(ehac)_2(eha)_2$ (ehac = 2-ethylhexylammonium carbamate; eha = 2-ethylhexylamine) was used as an Ag-precursor, whereas the usage of a salt such as $AgNO_3$ showed the formation of Ag nanoparticles in larger and irregular size (30 - 500 nm). The Ag nanoparticles (< 10 nm) prepared by using the Ag-complex could also be effectively stabilized by 1-amino-4-methylpiperazine. Transmission electron micrographs confirmed that the Ag particles were spherical and in the nanometer size.

Key Words: Ag Nanoparticles, 1-Amino-4-methylpiperazine, Multifunctional solvent

Introduction

The synthesis of metal nanoparticles with sizes ranging from 1 - 10 nm has recently been the focus of many studies due to their potential applications.[1,2] Silver nanoparticles (Ag-NPs) have received considerable attention in a variety of areas because of their unique antimicrobial properties,[3-5] especially in medical-related fields due to their potential for use in wound dressings, contraceptive devices, surgical instruments and bone prostheses.[6,7] To enable the production of nanoparticles on a large scale under simple and mild conditions, chemical approaches using series of reductants and stabilizers have been extensively developed.[8-16] The reducing and stabilizing abilities of the compounds used in such reactions may play an important role in the growth control of the metal nanoparticles. For example, a weak reductant and an electron-rich stabilizer may be favorable for control of the size and morphology of the metal nanoparticles obtained.[13-16]

Here, we report a new preparation method of Ag-NPs (< 10 nm) using 1-amino-4-methylpiperazine as a weak reducing agent and a solvating and stabilizing agent of nanoparticles. An Ag-complex such as $Ag_2(ehac)_2(eha)_2$ (ehac = 2-ethylhexylammonium carbamate; eha = 2-ethylhexylamine)[17-26] was used as an Ag-precursor. During stirring for 3 - 12 h at 50 °C, uniform Ag-NPs with sizes of < 10 nm were synthesized.

Experimental

Reagents and Analyses. 1-Amino-4-methylpiperazine (AMP) and $AgNO_3$ were obtained from commercial sources (Sigma-Aldrich or Merck) and used without further purification. An isopropyl alcohol solution of Ag-complex with 2-ethylhexyl amine and 2-ethylhexylammonium carbamate (Ag = 10 wt %) was purchased from InkTec Co., Ltd., Korea. Size and morphology of the as-prepared Ag-NPs were observed using a Philips TECNAI-FE12 transmission electron microscope (TEM, 120 kV). Briefly, the particles were dispersed in methanol, after

which a drop of the solution was placed on a carbon-coated copper grid and allowed to air-dry. The X-ray diffraction (XRD) patterns were recorded using a RIGAKU ROTAFLEX RAD-B diffractometer (Rigaku Corp., Japan) with Cu target Cu K1 radiation, a tube voltage of 40 KV and 60 mA in the range of 5 - 60°. Organic compounds were characterized by fast-atom bombardment mass spectroscopy (FAB-MS) (JMS-700, Jeol, Japan) and gas chromatography/mass selective detector (GC/MSD) (Varian 4000 instrument).

Synthesis of Silver Nanoparticles. 3.5 mL of Ag-complex or $AgNO_3$ solution in AMP in a range of 0.025 - 0.01 M was prepared and then stirred at 50 °C. After a few hours, the solution color changed yellowish and then brown, indicating the formation of Ag-NPs. The progress of the reaction was monitored periodically by UV-vis spectroscopy at 3, 6, 9, 12 and 24 h. Ag-NPs which were collected by centrifugation were characterized by TEM and XRD techniques.

Results and Discussion

The reducing ability of a reductant plays an important role in the size and morphology control of the metal nanoparticles obtained. AMP, which was utilized as a solvent, is a weak reducing agent as well as a good stabilizing agent. Two types of Ag compounds were employed as precursors, $AgNO_3$ as an inorganic salt and $Ag_2(ehac)_2(eha)_2$ (ehac = 2-ethylhexylammonium carbamate; eha = 2-ethylhexylamine) as an organometallic complex.

To monitor the growth of nanoparticles in AMP, the progress of the reaction was recorded periodically by UV-vis spectroscopy. In the presence of the Ag-complex in AMP solution and upon stirring, a rapid color change was observed from colorless to yellow or brown. As shown in the UV-vis spectra of Fig. 1, when the reaction time was extended to 6, 9, 12 and 24 h, the specific absorption which occurred at 403 nm in 3 h was slightly shifted to 422 nm and the intensity decreased to the level before the reaction. These findings indicate that the formation,
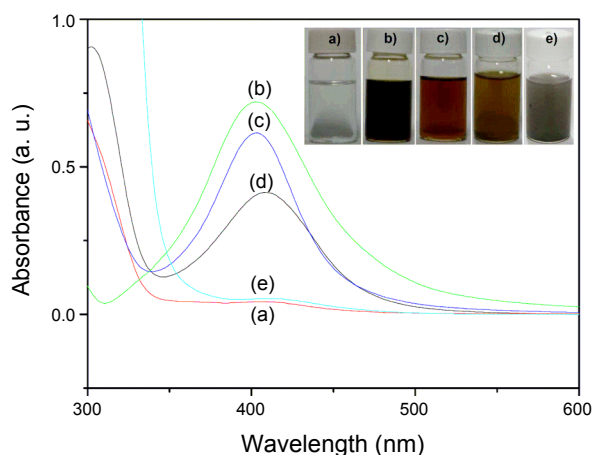
Figure 1. UV-vis spectra and photos of AMP solutions with Ag-NPs after reaction for (a) 0, (b) 3, (c) 6, (d) 12 and e) 24 h.
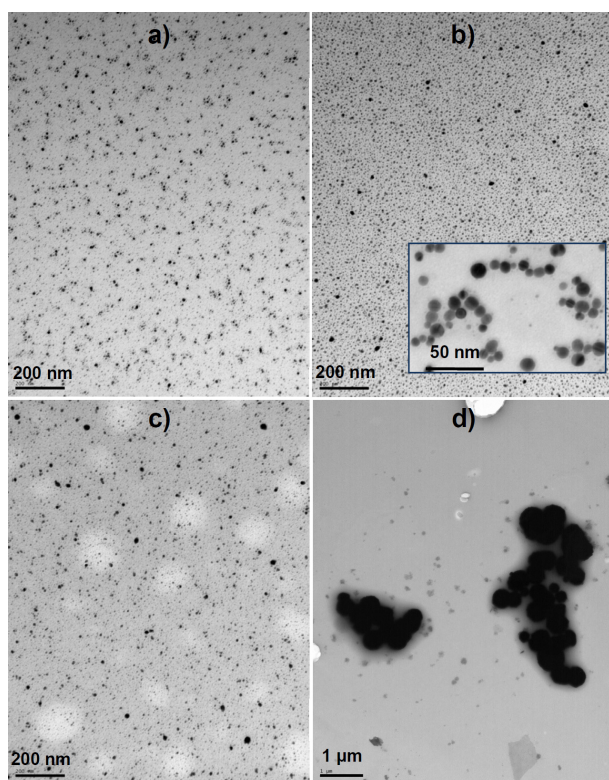

Figure 2. Transmission electron microscopic images of Ag-NPs prepared from Ag complex for (a) 3, (b) 6 and (c) 12 h and (d) from $AgNO_3$ after 12 h of reaction: Inset in (b) shows a magnified image of Ag-NPs formed after 6 h.

Figure 3. Size distribution (determined by calculation based on several TEM images) of Ag(0)-NPs prepared from (a) $Ag_2(ehac)_2(eha)_2$ and (b) $AgNO_3$ and (c) powder X-ray diffraction pattern of Ag(0)-NPs prepared from $Ag_2(ehac)_2(eha)_2$.

growth and precipitation of nanoparticles occurred, which could be confirmed in the photos in the inset of Fig. 1. However, upon changing the Ag-precursor to $AgNO_3$, more rapid growth and precipitation of nanoparticles was observed, which was confirmed through a rapid color change. This difference may have occurred because naked Ag(I) ions of $AgNO_3$ are surrounded directly by AMP molecules, which enables them to be easily reduced, whereas Ag(I) ions of Ag complexes are strongly coordinated with ligands such as 2-ethylhexylammonium carba-
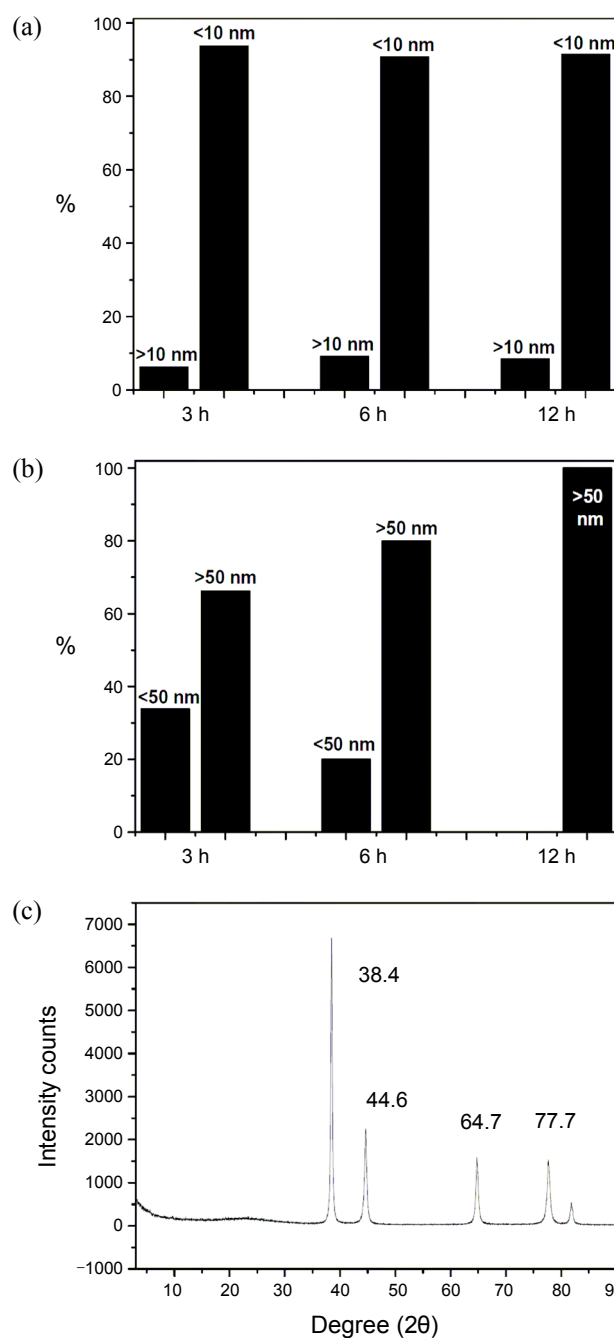
mate and 2-ethylhexylamine, even in AMP solution. When the reaction temperature increased to 50 °C, 2-ethylhexylammonium carbamate ligands on Ag(I) ions could be slowly decomposed to 2-ethylhexylamine and carbon dioxide, causing the Ag(I) ions to be exposed to AMP molecules.

TEM studies of Ag-NPs were conducted to evaluate the shape and size of the particles formed in the presence of $Ag_2(ehac)_2$ $(eha)_2$ and $AgNO_3$ after 3, 6, and 12 h. As shown in Fig. 2, spherical nanoparticles with a size less than 10 nm were generally
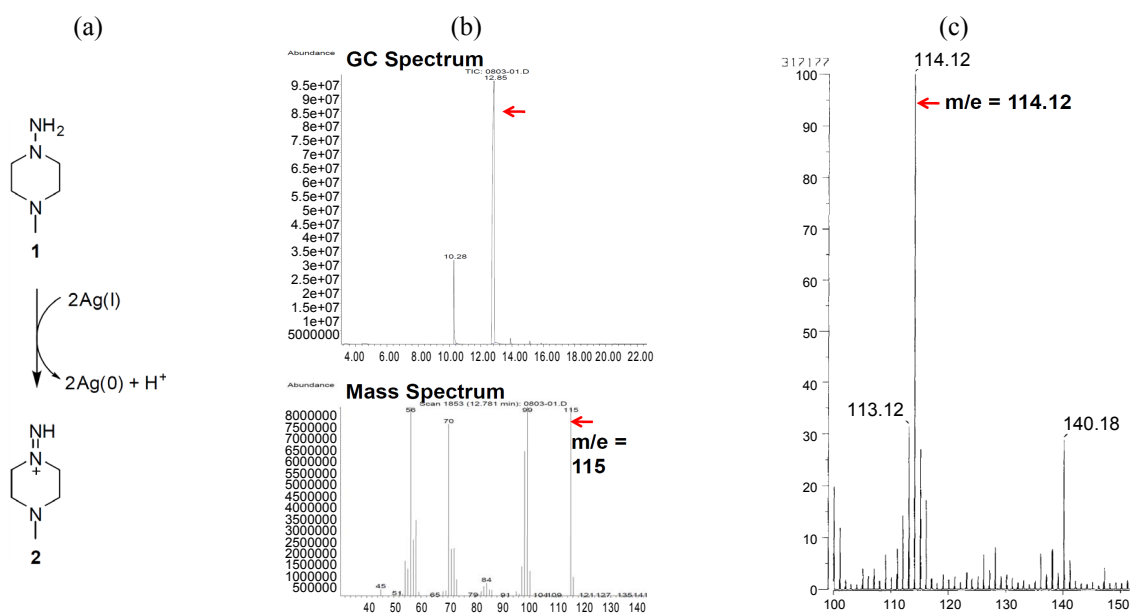
Figure 4. (a) Proposed mechanism for a role of 1-amino-4-methylpiperazine (**1**) in reducing Ag(I) ions, (b) GC-MS spectra of 1-amino-4-methylpiperazine **1** before the reaction and (c) FAB mass spectrum of the iminium ion **2** formed within the reaction mixture after 6h of the reaction.

formed between 3 - 12 h for the case of Ag-complex, whereas the formation of particles up to 500 nm was observed in the presence of AgNO₃. These results speak that the stability of the as-prepared Ag-NPs in the reaction condition can be strongly influenced by the molecule structure of Ag-precursor. When compared to various amine stabilizers (their single alkyl chains have 12 - 18 carbon atoms) employed in the previous studies,[15,16] AMP used in our experiment has very short alkyl chain. Nevertheless the uniform particles were formed after 6 h. However, the average size of the particles (< 10 nm) was relatively a little big than those (< 5 nm) prepared in the presence of amines with the longer alkyl chain length.

The particle size distributions were calculated based on the TEM studies for reaction times of 3, 6 and 12 h (Fig. 3a and b). To collect Ag-NPs and evaluate their powder X-ray diffraction pattern, the brown-colored reaction mixture produced from Ag-complex solution after 6 h of reaction was centrifuged and the upper phase was removed. The lower phase was diluted with new AMP and centrifuged again. This washing process was repeated several times. After allowing the concentrated solution to stand for several days, Ag-NPs were deposited on a glass, which was subjected to a powder X-ray diffractometer. The powder X-ray diffraction pattern of the nanoparticles showed peaks at 38.4, 44.6, 64.7, and 77.7°, confirming the presence of Ag(0) in the sample (Fig. 3c). Specifically, the peak at 38.8° with prominent peak counts confirmed the presence of Ag(0), which is the same as in the JCPDS cards.

Based on the observation and characterization of as-prepared Ag-NPs, we should assume that AMP molecules **1** play a role as a hydride donor. As proposed in Fig. 4, a hydride ion that might be detached from the primary amine to form an iminium ion **2**, reduces Ag(I) ion to Ag(0) specious. According to our assumption, we confirmed the formation of the iminium ion **2** by GC-MS and FAB mass spectroscopic methods (Fig. 4). The

FAB mass spectra of the reaction mixture after 6 h of stirring at 50 °C showed a prominent peak at $m/z = 114$, which corresponded to **2**, $C_5H_{12}N_3^+$, whereas the peaks related to AMP (**1**), $C_5H_{13}N_3$, at $m/z = 115$, were prominently observed in the GC-MS mass spectra.

Conclusion

We report here a new method for the preparation of Ag-NPs (< 10 nm) using AMP as not only a weak reducing agent, but also a solvating and stabilizing agent of nanoparticles. During stirring a silver complex such as Ag₂(ehac)₂(eha)₂ (ehac = 2-ethylhexylammonium carbamate; eha = 2-ethylhexylamine) in AMP at 50 °C for 3 - 12 h, uniform Ag nanoparticles with sizes of 2 to 10 nm were effectively synthesized, whereas from a silver salt such as AgNO₃ silver particles with sizes of about 30 - 500 nm were obtained. The prepared Ag nanoparticles (< 10 nm) could be effectively stabilized within the reaction solution of AMP as well. This method will be potential for use as a tool for preparation of metallic nanoparticles to enable control of the particle size in the nanometer scale as well as the uniformity of the particle size.

References

1. Lewis, L. N. *Chem. Rev.* **1993**, *93*, 2693.
2. Dupont, J.; Fonseca, G. S.; Umpierre, A. P.; Fichtner, P. F. P.; Teixeira, S. R. *J. Am. Chem. Soc.* **2002**, *124*, 4228.
3. Singh, M.; Sinha, K.; Mandal, R. K. *Mater. Lett.* **2009**, *63*, 425.
4. Yon, J. N.; Jamie, R. L. *Sci. Total Enviro.* **2008**, *400*, 396.

5. Jeon, H. J.; Yi, S. C.; Oh, S. G. *Biomaterials* **2003**, *24*, 4921.
6. Cohen, M. S.; Stern, J. M.; Vanni, A. J.; Kelley, R. S.; Baumgart, E.; Field, D.; Libertino, J. A.; Summerhayes, I. C. *Surg. Infect.* (*Larchmt*) **2007**, *8*, 397.
7. Fu, J.; Ji, J.; Fan, D.; Shen, J.; Biomed. J. *Mater. Res. A* **2006**, *79*, 665.
8. Ahmadi, T. S.; Wang, Z. L.; Green, T. C.; Henglein, A.; El-Sayed, M. A. *Science* **1996**, *272*, 1924.
9. Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. *J. Chem. Soc., Chem. Commun.* **1994**, 801.
10. Burshtain, D.; Zeiri, L.; Efrima, S. *Langmuir* **1999**, *15*, 3050.
11. Han, M. Y.; Quek, C. H.; Huang, W.; Chew, C. H.; Gan, C. M. *Chem. Mater.* **1999**, *11*, 1144.
12. Wang, J. G.; Neoh, K. G.; Kang, E. T. *J. Colloid Interface. Sci.* **2001**, *239*, 78.
13. Khanna, P. K.; Gokhale, R.; Subbarao, V. V. V. S.; Vishwanath, A. K.; Das, B. K.; Satyanarayana, C. V. *Mater. Chem. Phy.* **2005**, *92*, 229.
14. Li, Y.; El-Sayed, M. A. *J. Phys. Chem. B* **2001**, *105*, 8938.
15. Yamamoto, M.; Kashiwagi, Y.; Nakamoto, M. *Langmuir* **2006**, *22*, 8581.
16. Kashiwagi, Y.; Yamamoto, M.; Nakamoto, M. *J. Colloid Interface Sci.* **2006**, *300*, 169.
17. Park, M. S.; Lim, T. H.; Jeon, Y. M.; Kim, J. G.; Joo, S. W.; Gong, M. S. *Macromol. Res.* **2008**, *16*, 308.
18. Park, M. S.; Lim, T. H.; Jeon, Y. M.; Kim, J. G.; Joo, S. W.; Gong, M. S. *Sens. Actuators B* **2008**, *133*, 166
19. Park, M. S.; Lim, T. H.; Jeon, Y. M.; Kim, J. G.; Joo, S. W.; Gong, M. S. *J. Colloid Interface Sci.* **2008**, *321*, 60.
20. Lim, T. H.; Jeon, Y. M.; Gong, M. S. *Polymer(Korea)* **2009**, *33*, 33.
21. Jeon, Y. M.; Cho, H. N.; Gong, M. S. *Macromol. Res.* **2009**, *17*, 2.
22. Hong, H. K.; Gong, M. S.; Park, C. K. *Bull. Korean Chem. Soc.* **2009**, *30*, 2669.
23. Hong, H. K.; Park, C. K.; Gong, M. S. *Bull. Korean Chem. Soc.* **2010**, *31*, 1252.
24. Park, H. S.; Park, H. S.; Gong, M. S. *Polymer (Korea)* **2010**, *34*, 144.
25. Park, H. S.; Park, H. S.; Gong, M. S. *Bull. Korean Chem. Soc.* **2010**, *31*, 2575.
26. Park, H. S.; Park, H. S.; Gong, M. S. *Macromol. Res.* **2010**, *18*, 897.