Effects of Interior Wall on Continuous Fabrication of Silver Nanoparticles in Microcapillary Reactor

Shengtai He, Toshihiro Kohira,[†] Masato Uehara, Tugio Kitamura,[†] Hiroyuki Nakamura,
Masaya Miyazaki, and Hideaki Maeda*
Micro-space Chemistry Lab., National Institute of Advanced Industrial Science and Technology (AIST),
807-1 Shuku, Tosu, Saga, 841-0052
[†]*Department of Chemistry and Applied Chemistry, Faculty of Science and Engineering, Saga University,*
1 Honjo-machi, Saga, 840-5802

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After investigating the effects of the interior wall of the micro-capillary tube on the size distribution of silver nanoparticles, the well dispersed silver nanoparticles were fabricated continuously in a selected PTFE micro-capillary reactor with a one-step process.

In the past years, much attention has been paid on metal nanoparticles because of their fascinating electronic and optical properties and potential applications in catalysis, single electron tunneling devices, surface plasmon, and so on.[1–5] Because of their ability to sustain resonant collective electron oscillations excited in the near-ultraviolet or visible range of the electromagnetic spectrum,[6] silver nanoparticles have provided a particularly rich and ongoing focus for intense research. However, conventional methods are often impeded by their low production yields of nanoparticles, time consuming processing, and higher costs.[7,8] Micro-reactor technology has gained a great deal of attention in recent years.[9,10] With micro-reactors, the reaction is confined into a very small area (down to micro-scale), therefore, heat-transfer and mass transport are much more efficient. Such high heat and mass exchanging efficiency allows rapid heating and cooling with precisely defined residence times, in addition, such system also make it possible to decrease the mixing and diffusion time with reduced influence of mass transport on the rate of a reaction.[10] Thereby, a reaction is precisely controllable using a micro-reactor. In addition, continuous synthesis is a fundamental advantage of micro reactor technology. However, in many cases, deposition of products (or reactants) on capillary wall would degrade the properties of the products, engender a serious obstacle for continuous synthesis, and make it impossible to stably fabricate with this process. Therefore, in this study, we presented the fabrication of silver nanoparticles in a micro-reactor to investigate the effects of the interior wall, and then showed the advantage of micro-fluidic reactor to fabricate monodispersed silver nanoparticles continuously and stably.

Figure 1 depicts a schematic of the experimental setup. As a typical case,[11] silver acetate and oleylamine, with a molar ratio of 1:25, were dissolved in 1,2-dichlorobenzene (all reagents were purchased from Aldrich Chemical Co., Inc.); then the precursor solution was transferred into a syringe and injected into a capillary tube (i.d. = 500 nm) which was coiled and immersed into the 170 °C oil bath. The residence time of the reaction solution in the heating zone is adjustable by changing the flow rate. The fabricated silver particles were observed using a scanning transmission electron microscope (STEM: S5200; Hitachi Ltd.). X-ray diffraction and UV–visible spectra were examined using an X-ray diffractionmeter (PW 1820; Philips Co.) and a UV–visible spectrophotometer (UV-1601; Shimadzu Corp.), respectively. All samples for STEM and UV–visible spectra were washed with methanol and redispersed in chloroform except for the samples for the investigation of the effects of the tube wall.

To investigate the wall effects on particle size distributions, three capillary tubes with different surface properties were employed: (A) a fused silica tube with its interior wall modified with polyethylene glycol; (B) a non-modified stainless steel tube; and (C) a PTFE tube; and the same experiment was performed for the three capillary tubes. Figure 2a shows UV–visible

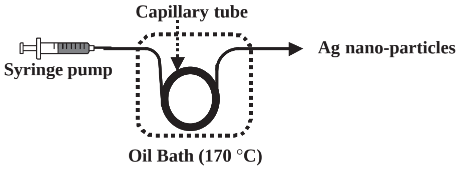

Figure 1. Schematic diagram of the experimental setup for the fabrication of silver nanoparticles in a micro-capillary reactor.

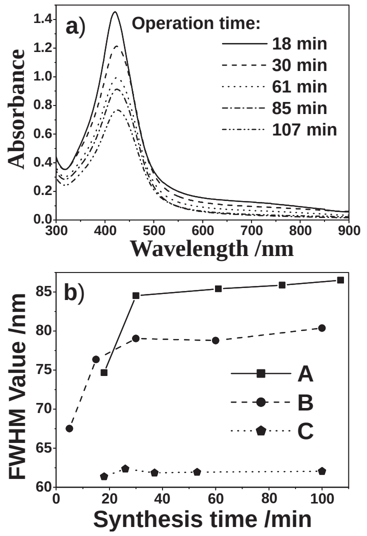

Figure 2. a) UV–visible spectra of silver nanoparticle colloids at different fabrication times with a reaction time of 3 min when a polyethylene glycol modified silica tube was used; and b) plots of corresponding FWHM values of absorption bands for a polyethylene glycol modified silica tube (A), a stainless steel tube (B), and a PTFE tube (C), respectively.

spectra of silver nanocrystals at various times during continuous synthesis when capillary A was used as a reactor. The plasmon peaks at around 414 nm become progressively weaker during the continuous fabrication, which shows that the concentration of silver nanoparticles decreases with time. After the reaction, the tube color has partly changed into black because of the deposition of silver nanoparticles. The absorption peak also shifts toward a higher wavelength in the continuous fabrication time of about 100 min, which means that the average particle size increases with time. These results demonstrate that with capillary A, despite the production of particle, a stable fabrication can not be attained. For capillary B, a red shift of the absorption peak was also observed (5 nm shift in 30 min) and peak intensity also decreased with time (minus 40% in 30 min), showing the same results as discussed above on capillary A. On the other hand, no deposition of silver nanoparticle was observed in the case of capillary C as depicted by non obvious change in the absorption peak location and intensity of the silver nanoparticles with continuous fabrication for 100 min. It can be argued that decrease in the concentration and increase in the particle size in cases of capillary A and B are due to the interaction (such as adhesion) between silver particles and the capillary walls during fabrication. Figure 2b shows FWHM values of absorption spectra of nanoparticles fabricated in those tubes. In the cases of capillaries A and B, the FWHM values increased to around 85 nm and 80 nm, respectively during continuous fabrication. For capillary C, its corresponding FWHM values were nearly stable with a low value of 62 nm. This result also shows that stable fabrication is possible only in capillary C in our experiment. For this phenomenon, some reasons including enhanced nucleation at the reactor surface and adsorption and desorption of the nanoparticles on the capillary wall can be considered. Nevertheless, it is evident here that the particle deposition on the tube wall decreases the yield, thereby increasing the particle size distribution. Consequently, the proper selection of the reactor surface is necessary for stable and continuous fabrication using this method.

From the above discussion, it is appropriate that PTFE tube should be selected to stably fabricate monodispersed silver nanoparticles. Figure 3 shows an STEM image of as-prepared silver nanoparticles with a reaction time of 3 min (flow rate of the precursor is 130 μL/min). The STEM image shows that well-dispersed silver nanoparticles with a size of 6.7 ± 0.5 nm were fabricated in a PTFE capillary tube with a standard deviation of less than 7.5%. In Figure 3, it can be seen that the ordered self-organizing structure formed in two dimensions because of the narrow size distribution. The corresponding XRD pattern and UV–visible spectra of as-fabricated silver nanoparticles are shown in Figure 4. By the Scherrer–Warren formula, the average particle size of the as-prepared colloids was inferred to be about 6 nm, which is nearly equal to the value counted from the STEM image.

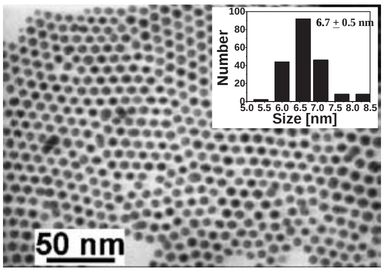

Figure 3. STEM image of Ag nanoparticles fabricated in a PTFE tube with a reaction time of 3 min (Insert: histogram showing the size distribution of silver nanoparticles).

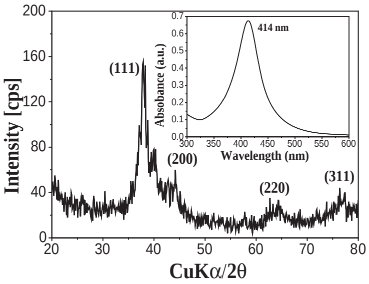

Figure 4. XRD pattern and UV–visible spectrum (inset) of silver nanoparticles fabricated in a PTFE tube with a reaction time of 3 min.

As reported previously, the reaction time can be controlled precisely by micro-reactor technique.[12] By changing the flow rate of the pumped precursor solution, nanoparticles with different sizes can be fabricated. In this experiment, when the precursor solution was pumped with flow rates of 79 μL/min and 56 μL/min (corresponding reaction times are 5 min and 7 min), silver nanoparticles with the sizes of 11.5 nm and 16.8 nm were fabricated. These results showed another case, as reported early for CdSe, to prepare nanoparticles with different sizes and narrow size distribution by precisely controlling the reaction with a micro-reactor.

In conclusion, the effects of the interior walls of capillary tube on the synthesis of silver nanoparticles were investigated in details. The results showed that high affinity between the particles and the reactor wall would result in low yield and wide size distribution. Subsequently, silver nanoparticles with a narrow size distribution were fabricated continuously in a PTFE capillary micro-reactor.

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