Preparation of Silver Nanoparticles from Silver(I) Carboxylate: Multicrystallity and Mechanisms

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The properties of nanomaerials can be differentiated significantly by controlling the crystallinity of the nanoparticles along with their sizes and shapes. The silver nanoparticles prepared from the decomposition of silver carboxylate reported to have multi-crystallinity even though their diameters were extremely small. This paper provides more detailed transmission electron microscopy and X-ray diffraction evidences for the 100 % existence of multi-crystalline silver nanoparticles, prepared from a facile one-pot organic phase synthesis and proposes a detailed silver nanoparticle growth mechanism based on these results.

Key Words: Multicrystalline, Silver nanoparticle, Silver carboxylate, Growth mechanism.

INTRODUCTION

Metal nanoparticles (NPs) have been studied extensively from both fundamental and industrial points of view[1]. In particular, the unusual properties and functionality of metal NPs, which are influenced strongly by their size being comparable to their electron mean free path, are attracting increasing attention. Recently, there have been many synthetic strategies for metal NPs with controlled size, composition and shape reported[2]. Tang and Ouyang[3] reported that the performance of NP-based devices can be differentiated significantly by controlling the crystallinity of NPs along with their sizes and shapes. Although many synthetic methods for size-controlled metal NPs have been published, only few reports revealed whether the prepared NPs are amorphous, multi-crystalline (MC) or single-crystalline (SC).

Recently, Nakamoto *et al*., reported the synthesis of Ag NPs from the decomposition of a specially designed coordinated compound, silver carboxylate, so called silver soaps, which are known to have a polymeric structure[4-11] (**Scheme-I**). A suspension of silver carboxylates in tertiary alkylamine solvents generate Ag NPs with a very narrow size distribution at elevated temperatures[8-11]. This synthetic route is so simple and reproducible that it can be used to prepare Ag NPs for industrial purposes. The formation of spherical particles with a mean diameter of 4.4 ± 0.2 nm (range 3.8-5.0 nm, based on TEM) was reported using silver myristate [$Ag(O_2C_{14}H_{29})$] and
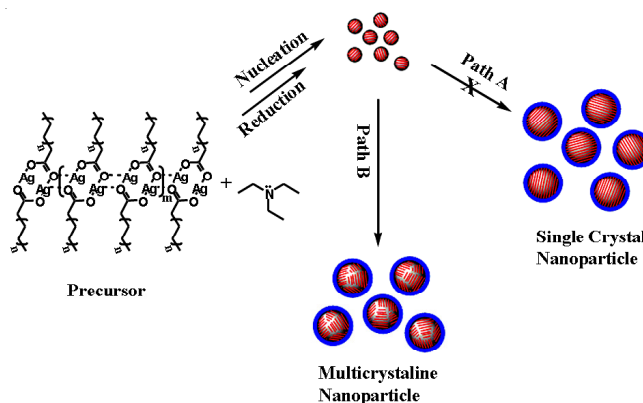
Scheme-I: Proposed growth pathway of seed silver NPs in a Sphere-like fashion

triethylamine (Et_3N). This result was further confirmed by XRD, showing broad peaks of a face centered cubic lattice of silver. The metal nuclei size was estimated to be 3.1 nm from the full width at half maximum (FWHM) of the XRD peaks fitted using the Scherrer equation. Although the average diameter estimated from TEM (4.4 ± 0.2 nm) and XRD (3.1 nm) are different, there are no reports of an explanation or further investigation.

To verify the discrepancy in the TEM and XRD results, this paper provides more detailed evidences for the 100 % existence of multi-crystalline Ag NPs, prepared from the

decomposition of Ag carboxylate complex. And a detailed Ag-NP growth mechanism is proposed based on these results.

EXPERIMENTAL

Silver nitrate (99.9 %) and triethylamine (98 %) were purchased from Aldrich and palmitic acid (extra pure) were provided by Duksan Chemical, Korea. The monodisperse Ag NPs were synthesized using the modified method reported in the literature[8]. Palmitic acid (2.8 g) was dissolved in triethyl-amine (40 mL) followed by the addition of AgNO₃ (1.8 g). After l0 min stirring, the solution turned out to be white slurry which was refluxed at 80 ℃ for 2 h. The synthesized Ag NPs were purified twice by addition of 40 mL acetone followed by centrifugation at 3500 rpm for 5 min. The heat treatment of the Ag(I) palmitate in triethylamine gave the identical results as described earlier, such as the size and crystallinity of prepared Ag NPs[8-11].

TEM and XRD measurements: A drop of the toluene suspension of the prepared Ag NPs was placed on a piece of carbon-coated 300-mesh copper grids (Ted Pella, Redding, CA, for TEM) and dried in the atmosphere. All HRTEM studies were performed with JEOL 2100F and 400FX field-emission TEMs and indicated the formation of regular shaped spherical particles with an average diameter of 6.8 ± 0.7 nm. (Fig. 1) to unambiguously characterize distinct crystallinity between single-crystalline and multi-crystalline-NPs, additionally the fast fourier transform (FFT) and XRD studies of synthesized NPs were performed. Powder X-ray diffraction data were collected at room temperature on a Bragg-Brentano diffrac-tometer (Bruker-AXS Endeavor D4) with a Cu X-ray tube (λ = 1.54184 Å) and a variable 6° slit. Data acquisition covered the angular range $15° \leq 2\theta \leq 140°$ at a step width of 0.02° and a counting time of 70 s per step.
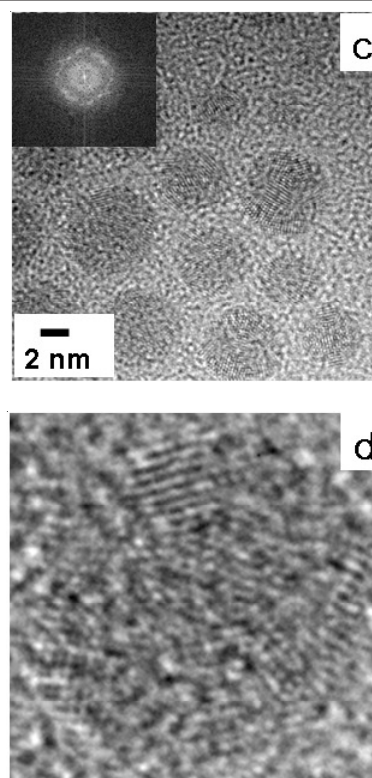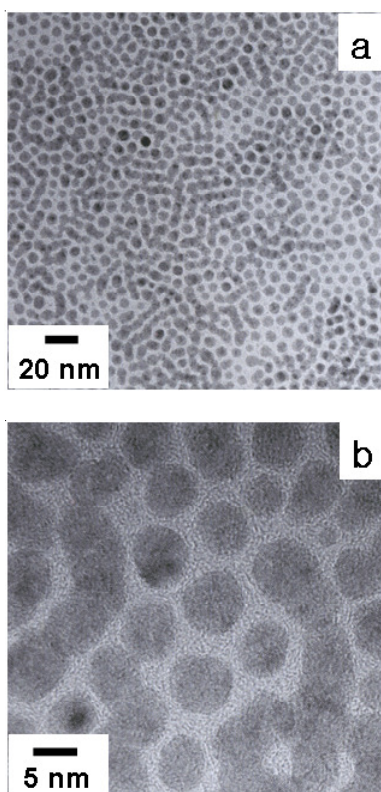
Fig. 1. HRTEM images of multi-crystalline Ag NPs. Inset in (c): the fast fourier transform pattern of a Ag NP

RESULTS AND DISCUSSION

The metathesis between sodium palmitate and AgNO₃ forms silver palmitate [Ag(O₂CC₁₅H₃₁)], which are known to have a polymeric structure[4-11] (**Scheme-I**). Two silver ions are bridged by two palmitates, generating eight-membered ring dimers [Ag₂(O₂CC₁₅H₃₁)₂], which are further linked by Ag-O bonds. The polymeric structure of silver soaps results from these four-membered rings[5-7]. Polymeric silver palmitate is insoluble in most solvents and forms a flocculent suspension with vigorous stirring. The Ag NPs were prepared by the reduction of silver carboxylate with a reducing agent, triethyl-amine, under mild conditions, *e.g.*, 80 ℃. The size (from 2.7-4.4 nm) of the Ag NPs was strongly affected by the alkyl chain length of the carboxylate and larger than the crystalline domain of the Ag NPs from the XRD analysis[8-11].

To verify the discrepancy in the TEM and XRD results of Ag NPs from the decomposition of silver carboxylate, this study examined the detailed reaction pathways and results using silver palmitate Ag(O₂C₁₆H₃₁) as a silver precursor complex. The palmitate ligand serve as nanoparticle-capping ligands and the NPs are generated by the reduction of Ag⁺ by Et₃N (**Scheme-I**).

Fig. 1 shows typical TEM images of the Ag NPs with an mean diameter of 6.8 ± 0.7 nm prepared from the precursor and Et₃N at 80 ℃ without subsequent size selection. High-resolution TEM (HRTEM) showed that all the NPs had distinct muti-crystallinity with a domain size of *ca.* 3 nm (Fig. 1d). This observation was further confirmed by fast Fourier trans-form (FFT). (Fig. 1c and its inset) FFT indicated that the crystallinity of the NPs is multiply twined based on the dots

inside the highlighted perimeter. However, the multi-crystallinity could be generated instantaneously by shining high energy electron beams, which is used in HRTEM and FFT. To clarify this issue, powder XRD pattern of the as-prepared Ag NPs (6.8 nm ± 0.7 nm) was obtained (Fig. 2), which agrees well with cubic Ag (ICSD # 64706)[12]. In order to derive crystallite-size information, Le Bail fitting[13] was performed by using TOPAS software[14]. The size for the domain of multi-crystals was calculated using FWHM values of each diffraction peak obtained during the fitting and the Scherrer formula[15]:
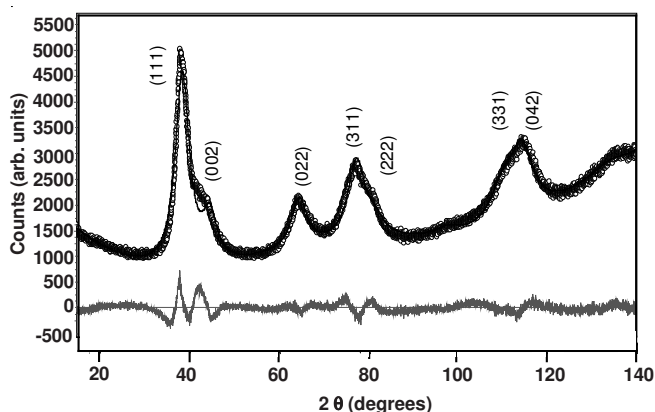

Fig. 2. Le Bail fitting profiles for Ag NPs recorded at room temperature. The circle line marks experimental points and the solid line is the calculated profile. The lower trace shows the difference curve and the ticks denote expected peak positions for cubic Ag

$$P = \frac{0.9\lambda}{(B\cos\theta_B)}$$

where P is the average particle size, B is FWHM in radian and θ_B is the Bragg angles. The calculated domain size of the Ag NPs was 2.5 ± 0.1 nm, indicating that the Ag NPs are composed of multiple SC domains. It should be noted that the estimated crystal size from the broadened XRD peaks is not the size of the NPs but the one of the single crystalline domains comprising the NPs. An analysis of the XRD and HRTEM results showed that MC Ag NPs, 6.8 nm in size with *ca.* 2.5 nm domains, had been prepared from a reaction between silver palmitate and Et₃N.

It is intriguing how the heat treatment of a mixture of AgNO₃ and Na(O₂C₁₆H₃₁) in Et₃N can generate multi-crystalline nanoparticles. A mechanism was proposed to account for the observed multi-crystalline Ag NP synthesis based on a better understanding of the crystallinity of the prepared Ag NPs (**Scheme-I**). When AgNO₃ and Na(O₂C₁₆H₃₁) are mixed in Et₃N, Ag⁺ and Na⁺ ions substitute for each other, generating a white dispersion of Ag(O₂C₁₆H₃₁) and NaNO₃. Upon heating the white dispersion up to 80 ºC, it turns brown (λmax = 420 nm), indicating that the Ag⁺ ions are reduced to Ag generating Ag NPs. The reduction of the generated precursor silver(I) palmitate by Et₃N can only occur at elevated temperatures, resulting in the nucleation of Ag NP seeds. Although its oxidation product is not well established, Et₃N is a weak reductant and has often been used in organometallic redox chemistry[16,17]. However, twinning planar defects are very difficult to avoid during the nucleation and growth steps of most noble metal

NPs without the addition of etchants, which can remove the metal twinning nuclei[18]. Chloride ions are often used as etchants in the synthesis of Ag NPs[3,19]. NO₃⁻ and ⁻O₂C₁₆H₃₁ anions do exist in the reaction solution and are not good etchants for multiple twinned nuclei. Therefore, without an efficient etchant of Ag, the rapid nucleation and growth from reduced silver palmitate can occur, followed by a self-focusing and slower Ostwald-ripening process to generate the multi-crystalline-NPs. Once the multi-crystalline-Ag-NPs are formed, the free palmitic acids liberated from the reduction of silver(I) palmitate surround the surface of the Ag NPs, preventing further growth.

Conclusion

In summary, the silver nanoparticles prepared from the reduction of silver(I) palmitate with Et₃N were multi-crystalline, 6.8 (0.7) in size and composed of 2.5(1) nm-sized crystalline domains. Disordered multiply twinned structures often form without additional etchants due to the lower surface and volume energies in sub-nano scale metal nuclei. Further studies into the synthetic routes of single crystalline silver nanoparticles from a reaction of silver carboxyate with amine and etchants are currently underway.

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