

## Particle Size Control of 11-Mercaptoundecanoic Acid-Protected Au Nanoparticles by Using Heat-treatment Method

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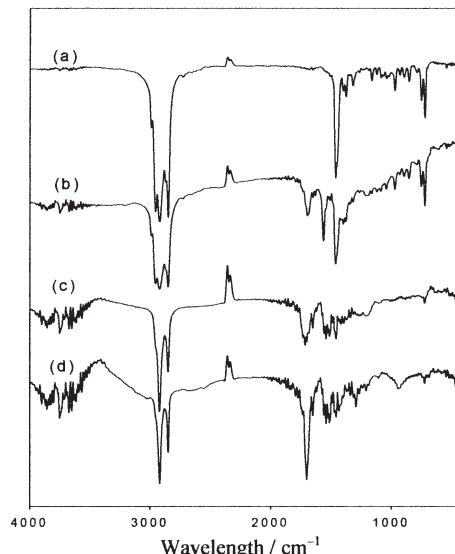
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Carboxylic acid-functionalized Au nanoparticles with very small and uniform core size (1.8 nm) could be prepared on the basis of the Brust's two phase method using 11-mercaptoundecanoic acid (MUA) as a surfactant. Various sizes of MUA-protected Au nanoparticles (MUA-Au) were obtained by the heat-treatment method in the solid state from 150 to 170 °C.

Nowadays there is a great interest in the formation of metallic nanoparticles aiming at their potential usage as advanced materials, e.g., new electronic, optical, and magnetic devices, and catalyst.<sup>1-3</sup> In 1994, the noteworthy preparative technique of alkanethiol-protected Au nanoparticles with about 2-nm core diameter was reported by Brust et al.<sup>4</sup> Leff et al. improved this technique to control a particle size by changing the Au/alkanethiol molar ratios, but the size distribution was slightly wide.<sup>5</sup> Reviewing previous relating studies to date, relatively simple 'straight alkyl chain' surfactants have been generally used as a particle stabilizer in one-pot synthesis; thus, we focused on adopting a stabilizer with a functional 'polar' group. The introduction of polar groups onto a particle surface is of interest to build structures with specified functions. Several groups reported Au nanoparticles protected by carboxylic acids.<sup>6-10</sup> However, facile preparation of small and monodispersed Au nanoparticles with polar functional groups is still challenging research target. Precise control of particle size is very important not only for fabricating the perfect superlattice of Au nanoparticles but also for investigating their size-dependent physical and chemical properties: e.g., superlattices with Au nanoparticles smaller and larger than about 2 nm would be applied to the single-electron tunneling devices<sup>11</sup> and nonlinear optical devices,<sup>12</sup> respectively. Here we have described the preparation of very small and monodispersed Au nanoparticles covered by 11-mercaptoundecanoic acid (MUA) with 1.8-nm core diameter in a one-pot synthetic method. In addition, we have succeeded to obtain a MUA-protected Au nanoparticle (MUA-Au) with various size from 1.8 to 9.8 nm by applying our original heat-treatment method in the solid state.<sup>13,14</sup>

Preparation of MUA-Au as a starting material for further heat treatment process was carried out on the basis of our previous procedure, only replacing dodecanethiol (DT) by MUA.<sup>13,14</sup> Briefly,  $\text{AuCl}_4^-$  dissolved in water was first transferred to a toluene organic phase by tetraoctylammonium bromide (TOAB), followed by addition of MUA and reduction process by aq  $\text{NaBH}_4$ . Then, 1 M aq HCl was added to adjust the pH value of 2.6 in water phase under vigorously stirring for 10 min. The reaction mixture was left quiet at ambient condition overnight.

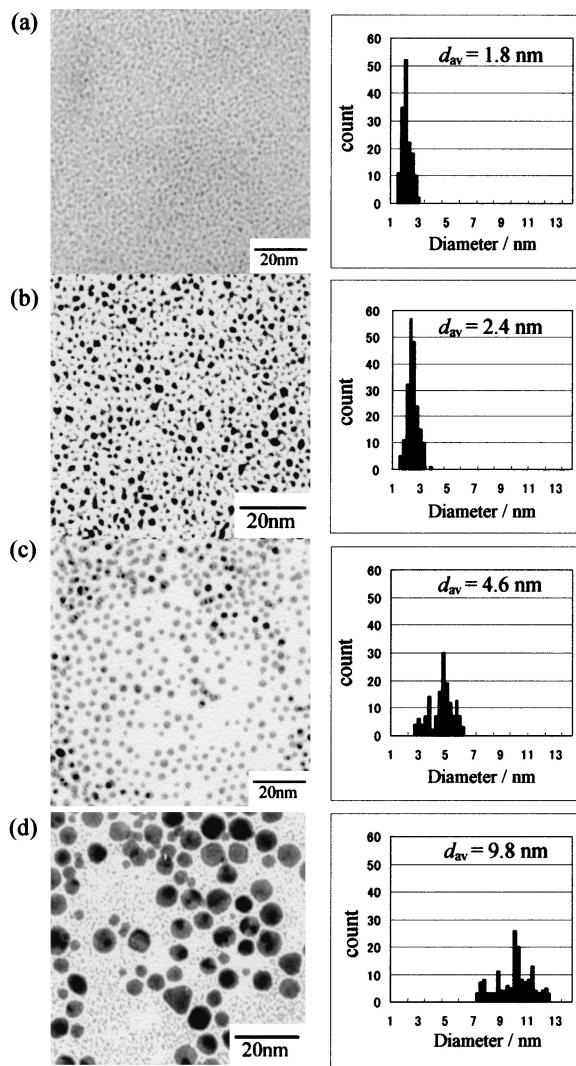
The black product deposited on an interface between organic and aqueous phase was then filtered off by a membrane, and dried in vacuum at room temperature for 1 day. The solid crude MUA-Au obtained by solvent evaporation of the reacted organic phase before pH treatment was heated in an electrical furnace at a prescribed temperature between 150 and 170 °C for 30 min in air. The product heat-treated at 150 °C was agitated in 1 M aq HCl. Other products were dissolved in 30 mL of toluene, mixed with 300 mL of methanol to be precipitated. The dark-brown powder was filtered off, washed with methanol to remove excess MUA and TOAB.



**Figure 1.** FT-IR spectra of (a) TOAB, (b) MUA-Au obtained without and (c) with pH treatment, and (d) MUA. MUA-Au obtained without pH treatment was prepared by purification of the crude MUA-Au particle in toluene/methanol.

The solubility of MUA-Au varied dramatically before and after pH treatment; namely, MUA-Au after pH treatment prefers to polar solvent (alcohol, alkaline water), while untreated MUA-Au to less polar solvent (toluene, chloroform). Considering this change due to the surface composition of MUA-Au before and after the purification by pH treatment, the FT-IR spectra are measured (Figure 1). The characteristic  $\text{CH}_2$  vibration peaks at 723, 1460, 2852, and 2922  $\text{cm}^{-1}$  as well as that of  $\text{CH}_3$  at 2954  $\text{cm}^{-1}$  of TOAB clearly appeared on curve (b), meaning that TOAB molecules cover the surface of MUA-Au before pH treatment. In contrast, the spectrum of MUA-Au after pH treatment is almost the same as that of MUA spectrum. Peaks at around

1700 cm<sup>-1</sup> in curve (c) assigned to the stretching vibration of the carbonyl groups of MUA dimer<sup>7</sup> are similar to that of pure MUA in curve (d); however, it is significantly different from those in curve (b) with a sharp peak at ca. 1600 cm<sup>-1</sup> assigned to carboxyl salts.<sup>7</sup> This also supports that an ammonium cation of TOAB was attached to carboxylic acid before pH treatment. The pH treatment effect for removing coordinated ammonium cations into carboxylic acid was also confirmed by XPS measurements. No peaks originating from N 1s (401.5 eV) were observed for MUA-Au after pH treatment. It should be noted that heat-treated MUA-Au also exhibits a sharp peak at ca. 1710 cm<sup>-1</sup> suggesting that carboxylic groups remain even after heat treatment. However, the peak intensity becomes smaller with increasing temperature because of slight decomposition of the adopted functional groups (vide infra).



**Figure 2.** TEM images and particle size distributions of (a) MUA-Au with pH treatment, heat-treated MUA-Au at (b) 150 °C, (c) 160 °C and (d) 170 °C. The scale bar in the TEM images is 20 nm.

The TEM images and size distributions of MUA-Au before and after the heat treatments are shown in Figure 2. At the beginning, MUA-Au with small and uniform average core diameter

( $d_{av}$ ) of  $1.8 \pm 0.3$  nm was obtained from the two-phase system. As for the size control by heating, the core diameter clearly grows by increasing heat-treatment temperature, being  $2.4 \pm 0.4$ ,  $4.6 \pm 0.8$ , and  $9.8 \pm 1.3$  nm at 150, 160, and 170 °C, respectively. UV-vis spectra of the prepared MUA-Au showed that the intensity of the absorption peak at ca. 520 nm originated from surface plasmon band increased with increasing heat-treatment temperature accompanied by a decrease in the peak width, supporting the particle size growth.<sup>15</sup> In the heat-treatment process, TOAB in the crude product plays a key role for particle growth since the monodispersed MUA-Au nanoparticles cannot be prepared without TOAB molecules. Presumably, TOAB with melting point at 95–98 °C serves as a solvent to stabilize MUA-Au during the aggregation process among particles. For further consideration of heat-treatment process, TGA analysis was performed. It indicates that weight loss extensively occurs above 190 °C mainly owing to combustion of organic layers. Between 100 to 190 °C in the heat treatment, a slight weight loss can be observed, inferring a little constructive change of organic ligands around particles (e.g. decomposition).

In summary, we have demonstrated the convenient synthesis and size control of Au nanoparticles with carboxylic groups by adopting a heat-treatment method in the solid state. The particle size was easily changeable from 2.4 to 9.6 nm only by heating with ionic surfactant of TOAB once small Au nanoparticles (1.8 nm) with functional groups were obtained at the beginning. Possible application such as ordered fixation of the prepared particles onto a substrate with specific chemical and physical properties depending on the adopted particle core size is under progress in our laboratory.

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