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Fusion and Growth Behavior of Gold Nanoparticles Stabilized by Allylmercaptane

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Summary: Fusion and growth behavior of gold nanoparticles in a relatively low temperature range were studied using a transmission electron microscopy (TEM). Using allylmercaptane (AM: 2-propene-1-thiol, $HS-CH_2-CH=CH_2$) as a particle stabilizer, a colloidal suspension of AM-terminated gold nanoparticles was prepared with a two-phase system. TEM observation revealed that the adjacent nanoparticles formed a particulate neck to give fused nanoproducts even at lower than 65 °C. Such fusion behavior allowed a non-spherical growth of the adjacent nanoparticles. Interestingly, the nanoparticle fused to form a nanowire-type structure when the thermal radical reaction occurred between the terminal double carbon bond of the stabilizer and the hydrogen terminated surface of silicon wafer.

Keywords: gold; growth; immobilization; nanoparticle; thiol

Introduction

Well-controlled nanostructure formed on a substrate plays a central role in development of nanotechnology.[1] Especially, low-dimensional array nanostructures have attracted much interest for producing the nanofabricated magnetic, electric, optical, and catalytic nanowires.[2] Effective researches have suggested that a colloidal dispersion of organically-stabilized nanoparticles is the most suitable starting material for building such hyper-structures.[3] However, it is difficult to transform in shape of the assembled nanoparticles to form a one-dimensional nanostructure by manipulating the individuals, because of some barriers including a steric or an electrical repulsion working between the adjacent molecular stabilizers attached to the surface of each particle.[3a] In the previous investigation, we reported here that 50 °C is a sufficient tempearture to occur the themal hydrosilyaltion between the alkene-cappted gold nanoparticles and hydrogen-terminated silicon (Si:H).[4] As a result, the nanoparticle was allowed to be immobilized on a silicon wafer via covalent Si-C linkage. Allylmercaptane (2-Propene-1-thiol or allylthiol) is the smallest stabilizer to achieve this immobilization. Gold nanoparticles stabilized by such small stabilizers often fused automatically when they are immobilized with a very small inter-particle distances. In fact, allylmercaptane-stabilized gold nanoparticles form a wirelike structure on the silicon surface even the immobilization was carried out at a very low temperature, e.g., 50 °C.[4] Another example is the thiocholine bromide-stabilized gold nanoparticle. These nanoparticles were highly positively changed and they could be densely adsorbed on DNA bundles, but they are immediately contacted and fused to grow up to form wirelike structures even at room temperature.[3c]

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Here, we would like to focus on allylmercaptane-stabilized gold nanoparticles treated at a moderately elevated temperature. TEM observations were carried out with these samples to understand the deformation and fusion of the nanoparticles. Wire-type structures of gold formed on silicon substrates were also found under careful AFM observation.

Experimental Part

Water was purified by Milli-Q system (> 18 MΩ cm). $HAuCl_4$ (Nakalai) was used as the metal source. As the stabilizing reagent, allylmercaptane ($HS–CH_2–CH{=}CH_2$: AM (2-propene-1-thiol or allylthiol), Tokyo Kasei) was selected. The AM-stabilized gold nanoparticles were prepared by the well-utilized Brust's two-phase process ($[Au] = 10$ mmol dm^{-3}, $[AM] = 20$ mmol dm^{-3}).[7] The reducing reagent was $NaBH_4$. The obtained particles were washed with water in order to remove the residues of the reducing reagent and the counter ions of the metal precursor. Then, the purified gold nanoparticles were re-dispersed into toluene. After heat treatment, TEM observation was carried out.

Immobilization of AM-stabilized gold nanoparticles on a hydrogen-terminated silicon surface was also carried out. The nanoparticles were immobilized by Si-C bond formation by thermal hydrosilylation between Si:H bonds and terminated C=C double bonds of AM.[6] The HF-treated silicon(100) wafer was immersed into the decane/toluene (4/1) dispersion of AM-stabilized gold nanoparticles.

Results and Discussion

Alkylthiols are very good stabilizing reagent for gold nanoparticles. Usually, thiols with a relatively long alkyl chain are used for the stabilizer. In our case, however, a very small molecule, 2-propene-1-thiol (AM) was selected. The molecular length of AM is as short as ca. 5.6 Å. A homogeneous colloidal suspension of AM-stabilzied gold nanoparticles could be prepared under the optimized condition. Despite the smallness in molecular-size of the stabilizing reagent, the gold nanoparticles could highly disperse in toluene without any precipitates as shown in the image in Figure 1. Figure 2 shows the particle size distribution of the ersultant AM-stabilized gold nanoparticles. The average diameter and its relative standard deviation of the particles were estimated to be 4.3 nm and 12.6%, respectively. In our previous study, the AM-stabilized gold nanoparticles were allowed to be immobilized on Si:H area by the reaction of terminal double carbon bond of the AM stabilizer with the Si-H bond on the basis of anti-Markovnikov fasion.[4] Interestingly, even at 50 °C, a grown structure of nanoparticles were observed. Such growth of the gold nanoparticels was not spherical. Simlar particle growth was also observed in the immobilization of hexenethiol (5-heptene-1-thiol)-stabilized gold nanoparticles at 100 °C. As a result, however, at 100 °C the hexenethiol-stabilized gold nanoparticles grew to form large spherical particles.[4b]

We next discuss the mechanism of such dimensional change of the nanonparticles under the heated condition. Figure 3 shows

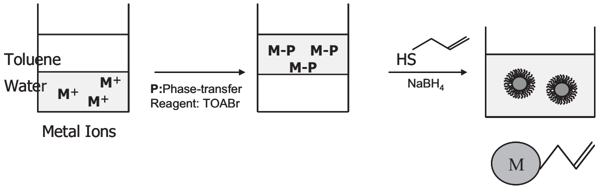

Figure 1.
Preparation procedure of 2-propene-1-thiol (AM)-stabilized gold nanoparticles.

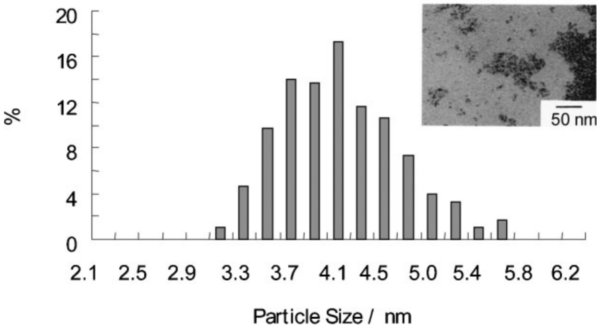

Figure 2.
Particle size distribution of AM-stabilized Au nanoparticles prepared at Au/AM = 1/2 (mol/mol). Inset: TEM image of the nanoparticles.

TEM images displaying the neck growth behavior between adjacent nanoparticles with increasing reaction temperature and time in toluene solution. As clearly seen in the image (a), a zero-dimensional nanoparticle was highly dispersed at 20 °C. Even at 40 °C, on the other hand, careful observation found some fusion with some adjacent nanoparticles. The previous study gave small improvement of of gold nanoparticles at 50 °C for 24 h.[4] These observations suggest that non-spherical sturcutre can be found in a low temperature range with a relatively short time. Although the TEM observation is limited, the adjacent spherical nanoarticles transformed into prolate ones with aspect ratios up to 2.5 (formation of short nanorods) through the neck-growth. Comparing Figures 3b with 3c and 3d, the neck-growth was enhanced with increasing reaction time and temperature. Figure 4 shows temperature dependence of the neck angles (θ), which mean interparticle angles between adjacent nanoparticles as shown in the inset. Althogh the distribution of θ is relatively large, the mean θ value increased with increasing enhanced with increasing reaction temperature. This phenomenon implies that the neck-growth occurs to yield the dimensional chnage, and is ehnanced with incleasing temperature.

In general, the melting point for the nanoparticle is much lower than that for the

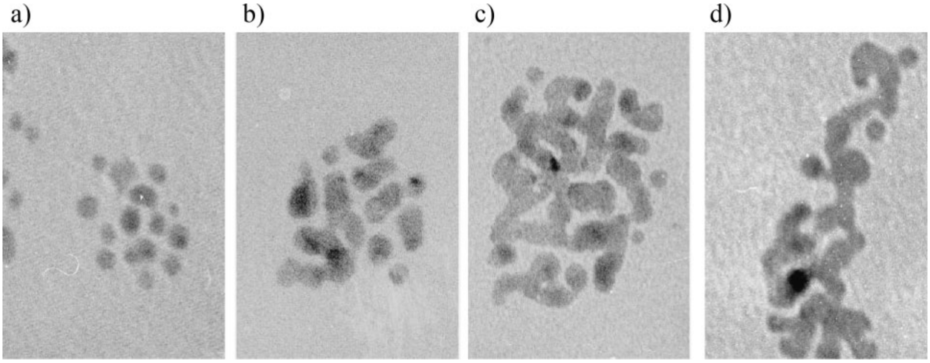

Figure 3.
TEM images showing shape transformation between adjacent Au nanoparticles in toluene with increasing reaction temperature and reaction time. (a) 20 °C for 30 min, (b) 40 °C for 10 min, (c) 40 °C for 30 min, and (d) 65 °C for 30 min. Inset gage: 10 nm.

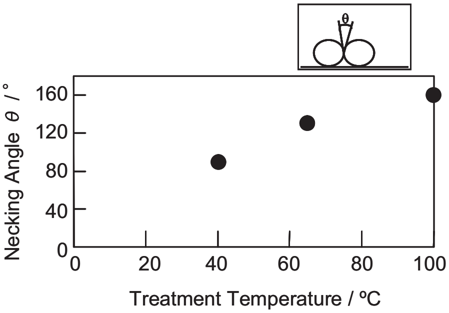

Figure 4.
The relationship between the mean neck angles (θ, obtained from TEM images) of thermally treated AM-stabilized gold nanoparticles and the reaction temperature.

bulk, and the heating-induced growth of metal nanoparticle without any stabilizers at lower temperature is also known (e.g., Ostwald ripening).[7] On the other hand, the stabilizers enable nanoparticles to keep the high dispersibility in solution up to higher temperature.[8]

Therefore, the stabilizer are generally removed at the intermediate synthetic step in the CdSe nanoparticle to nanowire transition.[8b] Maye, et al.[8d] have fabricated a ring structured ordering of Au nanoparticles with the average diameter of 5 nm by fusing through heating of the Au dispersed solution at 138 °C, and clarified no significant change in the shape of the nanoparticles below 110 °C. However, in this study, the careful observation of the TEM sample revealed the shape transformation of AM-stabilized gold nanoparticles occurred above 40~65 °C as shown in Figures 3. This is due to different chain lengths of the stabilizers used in between Maye's and our processes. Decanethiol was used in Maye's process while allylmercaptane was employed in our process. The hydrocarbon chains cannot stand straight above the surface in the case of the monolayer having less than eight carbons.[9] Additionally, an enormous tilted carbon chains might induce low density of stabilizers attached on nanoparticle surface. Thereby, the interparticle spacing among the particles should have been shortened in our process relative to Maye's process. These considerations would result in an

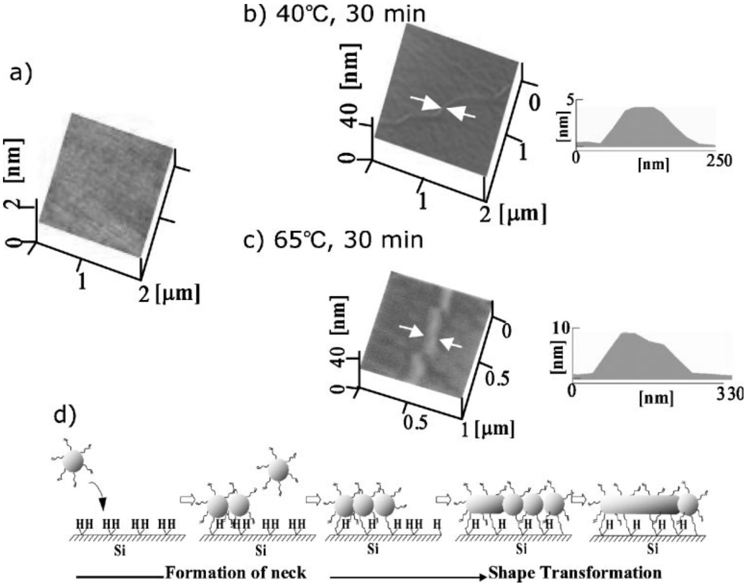

Figure 5.
AFM images of (a) cleaned hydrogen-terminated silicon (Si:H) surface, (b) after thermal hydrosilylation of AM-stabilized gold nanoparticles at 40 °C for 30 min, and (c) after thermal hydrosilylation of AM-stabilized gold nanoparticles at 65 °C for 30 min. (d) Schematic illustration of wire-type structure formation by immobilization of AM-stabilized gold nanoparticles onto the Si:H surface.

enhancement of the shape transformation at a lower synthetic temperature, although the detailed formation mechanism still needs further investigation.

On the other hand, one-dimensional wire-type structures were found on Si surfaces when AM-stabilized gold nanoparticles were immobilized onto hydrogen-terminated silicon surface. SEM observation in the previous studies could not find such wire-type structures.[4] Figure 5 shows AFM images of (a) the Si:H surface and typical wire-type structures of gold on the Si:H surface after thermal hydrosilylation of AM-stabilized gold nanoparticles on Si:H. The surface roughness of the Si:H was measured to be $\mathrm{RMS}_{\mathrm{Si:H}} = 0.16$ nm, which indicates the Si:H surface was extremely flat after cleaning. No particle was observed on Si:H surface. Under the reaction temperature of 20 °C, the Au nanoparticles were observed but they could be readily removed by ultrasonic rinse for 1 h in ethanol. But as shown in Figure 5b, a wire-type structure was observed on Si:H at 40 °C and its height was revealed as 4.6 nm which well corresponds to the particle diameter. According to the AFM tip convolution effect, the width observed in this figure was larger than the actual width. As shown in Figure 5c, both height and width of the wire-type structure formed at 65 °C were slightly larger than those observed in the 40 °C sample. This can be probably attributed to the enhancement of the neck-growth between adjacent nanoparticles on Si:H surfaces. Previous study showed that hydrosilylation of AM-stabilized gold nanoparticles at 50 °C for 24 h did not provide such wire-type structures.[4] The wire-type structure formation in this study can probably due to the accumulation of gold nanoparticles at step edges of the Si:H surfaces as shown in Figure 5d.

Conclusion

In conclusion, observation of low-temperature sintering of allylmercaptane (AM)-stabilized gold nanoparticles was carried out. At a very low temperature, Its structure could be formed through shape transformation of the self-assembled nanoparticles in one-dimension at low temperatures. This approach should be useful for manipulating individual nanoparticles in self-assembly on Si, because of controllable shape transformation by employing precise synthetic condition, such as chain length of the stabilizer reaction temperature and reaction time. Our proposed concept implies that the nanofabricated devices can be built on any substrates from solution by employing various kinds of nanoscale materials with the optimized monolayers, such as their length and terminated functional groups.

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