Room-Temperature Size Evolution of Thiol-Protected Gold Nanoparticles Assisted by Proton Acids and Halogen Anions

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Colloidal gold nanoparticles (Au NPs) have been attracting a wide interest because of their unique and fascinating optical, electronic, magnetic, and catalytic properties.[1−3] To obtain the monodisperse thiol-protected Au NPs, the post-treatment methods including the size evolution of alkanethiol-protected Au NPs in solution[4−6] and molten quaternary ammonium salt[7−9] in the temperature range from 110 to 250 °C have been reported. Because the post-treatment methods do not need the monodisperse starting NPs, they have a great potential for large scale synthesis. The post-treatment methods of thiol-protected Au NPs are quite important because the post-treatment methods of Au NPs protected by amine, phosphine, or other ligands, which are good candidates for ligand exchange by thiol, cannot provide the monodisperse Au NPs.[6] Although the post-treatment methods of thiol-protected Au NPs gives well-sized controlled NPs with a quite narrow size distribution, there are limitations in that the protective ligands with heat-labile functional groups or low boiling point cannot be used. Alternatively, both the controlled core nucleation and the following core growth during the one-pot synthesis of NPs can afford monodisperse Au NPs.[10−13] Since relatively strong reducing agents are requisite to control the nucleation and growth reaction in this one-pot synthesis, easily reducible protective ligands cannot survive under such a harsh condition. Here we report the size control of thiol-protected Au NPs under quite mild conditions with quaternary ammonium salt and proton acid at room temperature.

Dodecanethiol-protected Au (DT-Au) NPs that are 2.2 ± 0.3 nm in size (Figure 1a) were synthesized as seed NPs according to the report by Jana et al.[12] After repeated centrifugal purification, the DT-Au was dried under reduced pressure. Tetra-n-octyl-ammonium bromide (TOAB) and trifluoroacetic acid (TFA) were added to the freeze-evacuated dry toluene solution of DT-Au NPs at room temperature under N_2 atmosphere.[14] In the initial stage of the reaction, the seed DT-Au NPs evolved to form relatively polydisperse 4.8 ± 0.8 nm Au NPs (Figure 1b). Then size and size-dispersity became almost constant after the diameter of the DT-Au NPs reached about 6 nm (Figure 1c). The NPs of 6 nm are considered to be in a metastable state on the way of the reaction under this reaction condition. This size evolution reaction is not based on the dismutation of the Au NPs but on coalescence, because no smaller particles were observed in the reaction system. This size evolution also could be confirmed by UV−vis and XRD spectra, and the XRD results revealed that the grown DT-Au NPs were single crystal from the Scherrer's equation (Supporting Information, Figure S1).

The size evolution requires coexistence of TOAB and TFA. Toluene-soluble quaternary ammonium cations like di-n-dodecyldim-ethylammonium cation gave the similar size evolution results. Then the anion effect of quaternary ammonium salt on the size evolution was investigated by using tetra-n-octylammonium chloride and iodide
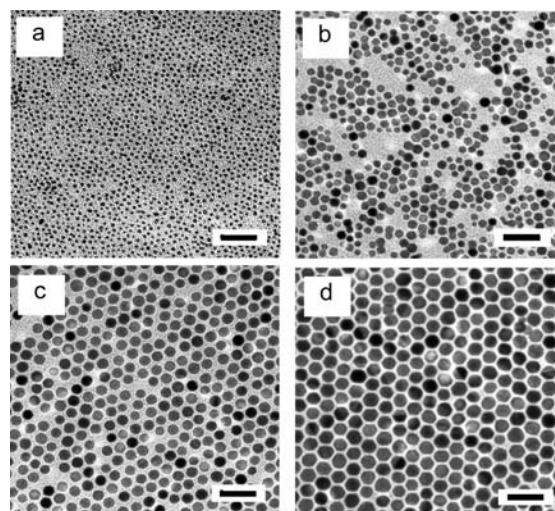

Figure 1. TEM images of (a) DT-Au seed NPs (2.2 ± 0.3 nm), acid treated DT-Au NPs (2 mM as Au atom) with TFA (40 mM) and TOAB (20 mM) for (b) 5 h at room temperature (rt) (4.8 ± 0.9 nm), (c) 75 h at rt (6.3 ± 0.6 nm), and (d) 21 h at 55 °C (7.8 ± 1.1 nm). The scale bar length is 20 nm.

instead of TOAB. Chloride ions slowed the size evolution reaction, that is, the seed DT-Au NPs grew to be 2.6 nm after 72 h at room temperature. On the other hand, the reaction rate was drastically accelerated by the iodide ions to generate not the size-controlled DT-Au NPs but only precipitate. From the viewpoint of hard−soft acid−base (HSAB) principle, the softer halogen anion easily interacts with the soft low-valent Au atom on the NP surface to promote the size-evolution reaction. It is well-known that the bromide anion of TOAB shows a certain adsorption ability to the Au NP surface to stabilize the Au NPs.[15,16] The reaction rate could be also controlled by changing the acidity of proton acids, TFA, trichloroacetic acid, and dichloroacetic acid, with pK_a values of 0.25, 0.65, and 1.3, respectively. The reaction rates were gradually decreased with increasing pK_a values (Figure S2), suggesting that the reaction is promoted by dissociating DT from the Au surface.
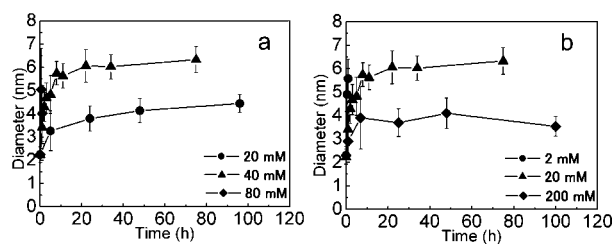

Figure 2. Size and size distribution changes of DT-Au NPs with (a) different concentrations of TFA (20−80 mM), DT-Au (2 mM as Au atom) and TOAB (20 mM), (b) different concentrations of TOAB (2−200 mM), DT-Au (2 mM as Au atom) and TFA (40 mM).

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Concentration effects of both TFA and TOAB on the size-evolution provide us with the important information on the reaction mechanism. Figure 2 shows the size evolution of the DT-Au NPs dependent on the concentrations of TFA and TOAB. The size of the DT-Au NPs could be controlled by changing the concentrations of TFA and TOAB to produce monodisperse 3.5−6 nm DT-Au NPs at room temperature. High concentration of TFA accelerated the reaction by dissociating DT from Au surface, and consequently size-controlled DT-Au NPs were not obtained at TFA concentration higher than 80 mM (Figure 2a). On the other hand, a larger amount of TOAB affords a slower reaction rate under the fixed concentration of DT-Au NPs and TFA, as shown in Figure 2b. It should be noted that the coalescence reaction cannot proceed in the absence of TOAB. These contradictory results can be elucidated by considering the roles that TOAB plays. One role is to initiate the dissociation of DT from the Au NPs surface through the nucleation reaction (details are presented later). Another role includes the passivation of Au NP surface. During the coalescence stage, Au NPs are partially protected by TOAB, which cannot adequately protect the Au NPs to lead fast coalescence. In the presence of a large amount of TOAB, the coalescence reaction is suppressed by well passivation of TOAB.

^{1}H NMR spectra of the reaction solutions were collected in order to reveal the reaction mechanism from the ligand side. Addition of either TFA or TOAB to the benzene-d6 solution of seed DT-Au NPs exhibited no significant ^{1}H NMR spectral change. When the seed DT-Au NPs were reacted with both TOAB and TFA, low concentration of free DT (2.18 ppm) and, interestingly, relatively high concentration of didodecyl disulfide (DDS, 2.58 ppm) were detected as proceeding the core growth (Figure S3). This result suggests that the adsorption−desorption equilibrium of DT on Au surface moves to desorption reaction by acid and bromide anion. The speculated reaction mechanism is presented as follows (Figure 3). At first, acidic protons interact with sulfur atoms of thiolates on Au surface. Then the bromide ions, which have an appropriate affinity to Au surface, interact with DT-Au NP surface, followed by dissociation of DT on Au. A redox reaction must be considered for the formation of DDS. The oxidation of thiolates was not be induced by oxygen, because the sample was strictly freeze-evacuated, N_2-substituted, and sealed. It was also confirmed that TFA and TOAB did not oxidize DT in the absence of DT-Au NPs. Considering the formal charge of S(−1) and Au(+1) of the S−Au bonds on DT-Au NP surface, the redox reaction between Au(+1) and S(−1) may proceed by the aid of already desorbed DT to form Au(0) and DDS, in which fairly unstable Au(0) surface is briefly protected by bromide anions. Finally, the coagulation between unstable Au(0) surfaces leads the core growth to form the metastable DT-Au NPs. The longer reaction time is responsible for higher concentration of DDS. This reaction mechanism is consistent with the concentration effects of TFA and TOAB mentioned above. Actually, XPS measurement revealed that the atomic ratio of S/Br of as prepared size-controlled DT-Au NPs shown in Figure 1c was ∼4, indicating that the surface thiolates were substituted by bromide anion.

When the reaction was carried out under a mild heating condition at 55 °C, the diameter of DT-Au NPs reached 8 nm (Figure 1d), this size being close to the solubility limit for DT-Au NPs in toluene. This result indicates that the final size of Au NPs can be widely controlled by the reaction temperature. Compared with our previous report (the temperature over 200 °C is needed to obtain 8 nm DT-Au NPs),[8] it will be seen that this proton acid-mediated method is far more likely to be versatile. Furthermore, this mild acid method can be applied to thiols with functional groups sensitive to reducing agent, basic
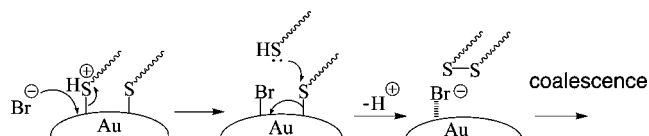

Figure 3. Schematic illustration of acid-assisted and bromide anion-assisted coalescence mechanism of DT-Au NPs.

condition, and heat. Tridecyl 3-mercaptopropanate (TDMP) was chosen as a ligand sensitive to the reducing agent. Seed TDMP-protected Au NPs with 2.5 ± 0.5 nm in size (5 mM as Au atom) grew to be 4.3 ± 0.5 and 5.4 ± 0.7 nm after the reaction with TFA (100 mM) and TOAB (50 mM) at room temperature for 44 and 267 h, respectively (Supporting Information, Figure S4). The IR spectra of carbonyl groups (∼1630 cm^{-1}) of size-controlled TDMP-Au NPs were similar to those of seed TDMP-Au NPs and TDMP molecule itself, indicating that the NPs grew without changing the structure of TDMP (Figure S5). Hexanethiol-protected Au (HT-Au) NPs could not be controllably evolved at room temperature because of the intrinsic instability of HT-Au NPs. However, the uniform size evolution of HT-Au NPs was achieved at 10 °C (Figure S6).

In conclusion, a mild size control method for thiol-protected Au NPs was developed. When thiol-protected Au NPs were reacted with TFA and TOAB, the size of Au NPs was tuned in the range from 2 to 8 nm at 10−55 °C. Because of the mild reactivity of acids and bromide ions to organic ligands, various thiols sensitive to heat, base, and reducing agent can be utilized for this method.

Supporting Information Available: Procedure for the size-evolution reaction of DT-Au NPs, UV−vis, and XRD spectra of DT-Au NPs, size and size distribution changes of DT-Au; ^{1}H NMR spectral changes during the reaction; TEM images of TDMP-Au NPs; IR spectra of TDMP; seed TDMP-Au NPs; and TDMP-Au NPs; TEM images of HT-Au NPs. This material is available free of charge via the Internet at http://pubs.acs.org.

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