Electronic Supplementary Information

Ultrafast, 2-minute Synthesis of Monolayer-Protected Gold Nanoclusters (d<2 nm)

Matthew N. Martin,[a] Dawei Li,[a] Amala Dass,[b] and Sang-Kee Eah*[a]

Department of Physics, Applied Physics, and Astronomy, Rensselaer Polytechnic Institute, Troy, New York 12180,USA,Department of Chemistry and Biochemistry, University of Mississippi, University, Mississippi 38677, USA

* Corresponding author: SangKeeEah@gmail.com; phone, (518) 276-3972; fax, (518) 276-6680.
[a] Rensselaer Polytechnic Institute. [b] University of Mississippi.

Experimental Details

Materials: the following chemicals were used as obtained: $HAuCl_4{\cdot}3H_2O$, $NaBH_4$ granules, 1.0 N HCl solution, 1.0 N NaOH solution, 1-hexanethiol, 1-dodecanethiol, 4-methylbenzenethiol, 3-mercaptopropionic acid, and 4-mercaptobenzoic acid from Sigma-Aldrich; methanol, hexane, and toluene from VWR. Deionized (DI) water with resistivity of 18.2 MΩcm was used. 40 mL KG-33 borosilicate glass vials from Kimble-Kontes were used after cleaning with DI water, acetone, hexane, and being heated at 540 °C. No rigorous (or dangerous) cleaning material such as aqua regia or a hydrofluoric/nitric acid mixture was used for glasswares.

Preparation of the reagent stock solutions: an aqueous stock solution of 50 mM $AuCl_4^-/2H^+/Cl^-$ ions in a glass vial was made by dissolving $HAuCl_4{\cdot}3H_2O$ powder with the same molar amount of HCl using a 1.0 N HCl solution, which was stable for more than several months. An aqueous stock solution of 50 mM $BH_4^-/OH^-/2Na^+$ ions in a plastic beaker or a glass vial was made by dissolving $NaBH_4$ granules with the same molar amount of NaOH using a 1.0 N NaOH solution, which was stable for several hours at room temperature and several days if the container was sealed from CO_2 molecules in the air. [S1] Therefore, cooling the borohydride solution or using a freshly made borohydride solution was not required. A hexane stock solution of 1-hexanethiol, 1-dodecanethiol, or 4-methylbenzenethiol was made at the concentration of 5.0 μmol per 6.7 mg, or 500 mM. By using these stable stock solutions, ultrafast synthesis could be repeated as many times as possible to check the reproducibility by getting an identical UV-VIS spectrum. Finding the right conditions for controlling the diameter of gold nanoclusters <2 nm could be done fast and easily via many reproducible repetitions.

Ultrafast, 2-minute synthesis of gold nanoclusters: First, 6.7 mg of hexane containing 5.0 μmol of 1-hexanethiol was added to 5 g of methanol in a glass vial as shown in Figure 1 of the main text. Next, 100 μL of water containing 5.0 μmol of $AuCl_4^-/2H^+/Cl^-$ ions was added to the vial, changing its color to light yellow. Then, 300 μL of water containing 15 μmol of $BH_4^-/OH^-/2Na^+$ ions was added all at once. The solution's color was changed from light yellow to brown in <1 second, indicating formation of gold nanoclusters and capping (growth stop) by thiol. The solution's color changed into black within a few tens of seconds due to precipitation of hexanethiolate-coated gold nanoclusters in mostly methanol. After adding 5 g of hexane, the vial was shaken for 30 seconds to extract only hexanethiolate-protected gold nanoclusters to the hexane top phase with nearly 100% efficiency and leave all the reaction byproduct ions in the mostly methanol bottom phase. Thanks to the two immiscible liquids of methanol and hexane, no post-synthesis cleaning was necessary with just one impurity of free, unreacted alkanethiol molecules in the hexane solution of gold nanoclusters. The whole process took <2 minutes.

The stably dispersed hexanethiolate-coated gold nanoclusters in hexane were checked for their diameter with a UV-Vis spectrophotometer (Shimadzu, double beam).

MALDI-TOF mass spectrometry: the hexanethiolate-coated gold nanoclusters were dried by evaporating hexane, sent from RPI to Mississippi, redispersed in hexane, and characterized by MALDI-TOF mass spectrometry.[S2] Mass-spectra were obtained using a Bruker Autoflex equipped with a nitrogen laser. 3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) was used as the matrix with 1:1000 analyte:matrix ratio. 2 μL of the mixture was applied to the target and air dried.

Poor solubility of hexanethiolate-protected gold nanoclusters in methanol

The mostly methanol solution changes its color from initially brown to black in a few minutes, since hexanethiolate-protected gold nanoclusters are not soluble in methanol. The precipitated gold nanoclusters at the bottom of the glass vial are shown in Fig. 1S. Once "naked" gold nanoclusters are coated with a monolayer of alkanethiolate molecules, the gold cores do not touch each other and therefore the aggregation is reversible. Therefore, they are completely redispersed in a non-polar solvent such as hexane or toluene. We choose the pair of methanol and hexane, since these two solvents are immiscible with each other. Note that methanol is miscible with toluene. Instead of considering methanol as a bad solvent due to the precipitation, we exploited its property as an intermediate solvent between water and non-polar solvents due to reversible aggregation and re-dispersion of monolayer-protected gold nanoclusters. All reactions of gold ions' reduction, nanocluster formation, and thiolate-coating happen very fast in <1 second, which must be challenging to characterize and understand. A theoretical study for the ultrafast and complex processes might be better than an experimental one for understanding how thiol ligands react with gold ions, neutral gold atoms, and "naked" gold nanoclusters in the mixture of mostly methanol, little water, and very little hexane.

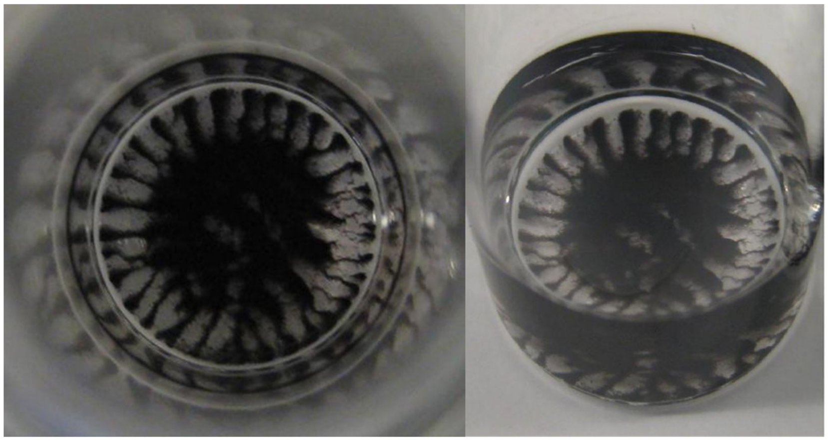

Figure 1S. Photographs (two viewing angles) of precipitated hexanethiolate-protected gold nanoclusters in the mostly methanol mixture several minutes after their formation. These aggregated nanoclusters are completely redispersed in hexane after phase-transfer.

Slow reaction of gold ions with 1-hexanethiol in methanol

The mixture of 5 g of methanol, 100 mg of water, and 6.7 mg of hexane containing $AuCl_4^-/2H^+/Cl^-$ ions and 1-hexanethiol molecules, is of light yellow color due to Au(III) ions as shown in Fig. 2S. However, the same solution changes its color to cloudy white after overnight aging, implying that Au(III) ions react with 1-hexanethiol molecules very slowly. Note that Au(III) ions in water react with water-soluble thiol molecules such as 3-mercaptopropionic acid or 4-mercaptobenzoic acid very fast, changing the aqueous solution's color from light yellow to cloudy white in <10 seconds. After slow reaction for 5 min, the mostly methanol solution's light yellow color does not noticeably change.

However, the diameter of hexanethiolate-coated gold nanocluster/nanoparticles becomes larger, d<3 nm in comparison to d<2 nm for the minimum reaction time, as shown in Fig. 2 of the main text. We also checked that gold nanoclusters (d< 2 nm) don't form with the cloudy white solution. Unlike other synthesis methods for gold nanoclusters in the literature, minimizing this reaction is key to controlling d<2 nm in our new ultrafast synthesis method. We speculate that "naked" gold nanoclusters are first formed and then later hexanethiolate-coating follows, even though we cannot observe this separation of nucleation from stabilization in time during the ultrafast reaction in <1 sec.

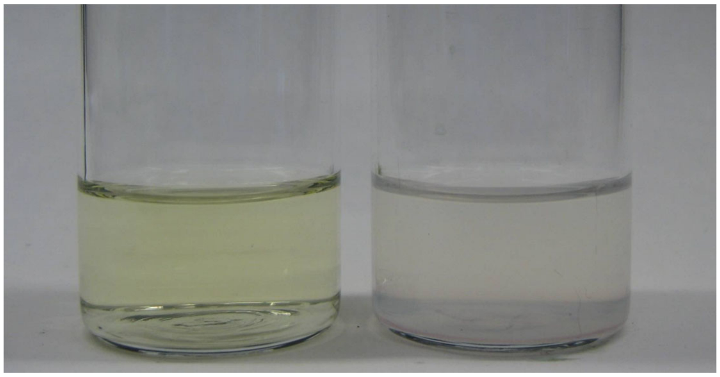

Figure 2S. Photographs of 1-hexanethiol molecules and $AuCl_4^-/2H^+/Cl^-$ ions in the mixture of 5 g of methanol, 100 mg of water, and 6.7 mg of hexane right after the addition (left, light yellow) and after overnight reaction (right, cloudy white). On the contrary, the reaction of Au(III) ions with water-soluble thiol molecules in water is much faster and takes <10 sec.

"Sweet zone" for complete reduction of all the gold ions

As with "naked" gold nanoparticles in water without any stabilizer, we discovered the same "sweet zone" for hexanethiolate-coated gold nanoclusters. In water, the ratio of $BH_4^-/OH^-/2Na^+$ ions to $AuCl_4^-/2H^+/Cl^-$ ions in water must be equal to or larger than 300 % molar amount of gold ions for simultaneous reduction of all gold ions in <1 second and generating nearly monodisperse "naked" gold nanoparticles without any stabilizer.[S1] The size uniformity may be due to the separation of the initial fast nucleation from the later slow growth via coagulation. As shown in Fig. 4 of the main text, UV-Vis spectra clearly show that the boundary exists between 200 and 300 %, above which we obtained an identical spectrum at both 300 and 400 %. Each borohydride ion (BH_4^-) with 4 hydride (H^-) arms can ideally reduce one Au^{3+} ion completely. It is tempting to predict that 100 % BH_4^- ions can reduce all the gold ions. However, the actual reaction stoichiometry is quite complex due to the presence of excess H^+ and OH^- ions, which we don't fully understand, especially the dynamic progression as a function of time. We don't have a clear understanding why the boundary must be between 200 and 300 %. The photograph of the 100 % case shows that the methanol phase is not completely colorless but faintly yellow, meaning that not all gold ions are reduced to neutral gold atoms and eventually "naked" gold nanoclusters. The UV-Vis spectrum for the 200 % case shows the absorbance at wavelengths >~600 nm becomes larger than that of the identical 300 and 400 % case. This means that there are polydisperse gold nanoclusters/nanoparticles in the hexane phase. In water, polydisperse "naked" gold nanoparticles are obtained for a ratio below the boundary, while nearly monodisperse ones within the "sweet zone".[S1] We note that "naked" gold nanoparticles without thiol molecules grow and precipitate very rapidly in a mixture of methanol and water. From this observation of the same "sweet zone", we infer that the same fastest reaction of nanocluster formation in <1 sec is followed by growth into nanoparticles in water and alkanethiolate-coating with no growth in mostly methanol respectively.

Trapped gold nanoclusters/nanoparticles at the methanol-hexane interface due to excess thiols

Using hexanethiol molecules more than 100 % molar amount of gold atoms resulted in more trapping of gold nanoclusters/nanoparticles at the methanol-hexane interface, as shown in Fig. 3S. Also, hexanethiol molecules less than 75 % resulted in d<3 nm. Currently, we don't fully understand why more 1-hexanethiol molecules make the phase-transfer less efficient due to the liquid-liquid interface trapping.

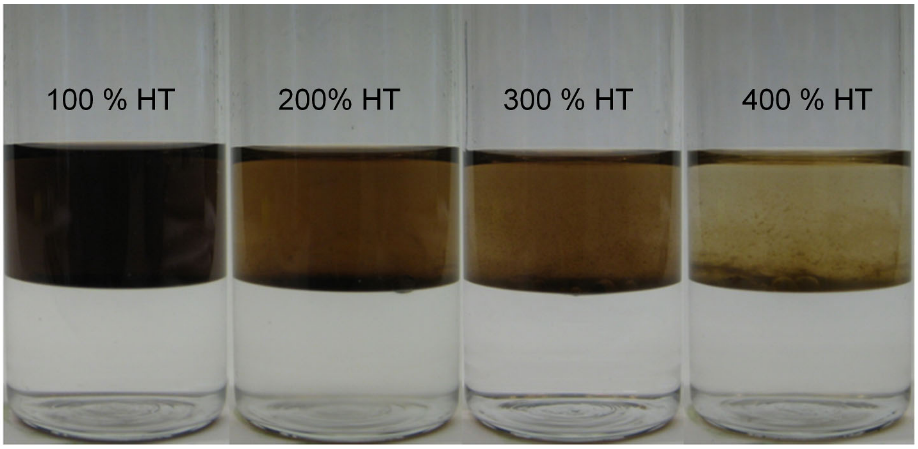

Figure 3S. Using 1-hexanethiol (HT) more than 100 % molar amount of gold atoms causes more gold nanoclusters/nanoparticles to be trapped at the liquid-liquid interface.

References

[S1] "Charged Gold Nanoparticles in Non-Polar Solvents: 10-min Synthesis and 2D Self-Assembly", Martin, M. N.; Basham, J. I.; Chando, P.; Eah, S.-K. *Langmuir* **2010**, *26*, 7410-7417. http://dx.doi.org/10.1021/la100591h

[S2] "Nanoparticle MALDI-TOF Mass Spectrometry without Fragmentation: Au25(SCH2CH2Ph)18 and Mixed Monolayer $Au_{25}(SCH_2CH_2Ph)_{18-x}(L)_x$", Dass, A.; Stevenson, A.; Dubay, G. R.; Tracy, J. B.; Murray, R. W., *J. Am. Chem. Soc.* **2008**, *130,* 5940-5946. http://dx.doi.org/10.1021/ja710323t