

Supporting Information

**Formation of Uniform and High-Coverage Monolayer Colloidal Films of
Midnanometer-Sized Gold Particles over the Entire Surfaces of 1.5-in. Substrates**

Sayaka Yanagida^{*,1,2}, Satoko Nishiyama¹, Kenji Sakamoto^{*,1}, Hiroshi Fudouzi¹, and
Kazushi Miki^{*,1,3,†}

¹ National Institute for Materials Science (NIMS), 1-1 Namiki, Ibaraki 305-0044, Japan

² Center for Crystal Science and Technology, University of Yamanashi, 7-32 Miyamae,
Kofu 400-8511, Japan

³ Faculty of Pure and Applied Sciences, University of Tsukuba, 1-1-2 Tennodai, Tsukuba,
Ibaraki 305-8571, Japan

[†] Present address: Department of Electrical Materials and Engineering, Graduate school
of engineering, University of Hyogo, Shosya 2167, Himeji, Hyogo 671-2280, Japan

E-mail: sysanagida@yamanashi.ac.jp; SAKAMOTO.Kenji@nims.go.jp;
miki@eng.u-hyogo.ac.jp,

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Preparation of alkanethiol-capped gold nanoparticles (AuNPs)

Prior to use, all glassware and magnetic stirring bars were soaked in a fresh aqua regia solution for about an hour. Subsequently, they were rinsed 10 times with Milli-Q water and dried in an oven at 80°C. All plasticware was also washed sequentially with hot tap water and then Milli-Q water, and then dried in an oven at 80°C. AuNPs of 14, 34, 67 nm in diameter were synthesized by the seed-mediated growth method [1]. The 14-nm AuNPs were obtained as Au seeds, and the larger AuNPs were obtained by growing the seeds. The Au seeds with a size distribution of $d = 14 \pm 1$ nm was synthesized by reduction of chloroauric acid as follows. 20.0 mL of a 0.50 mM aqueous $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ solution was refluxed for 15 min while stirring constantly, and then 1.0 mL of a 38.8 mM aqueous sodium citrate solution was added to the solution, which caused a change in solution color from pale yellow to deep red. After the reflux was further continued for 20 min to complete the reaction, a colloidal solution of citrate-capped Au seeds was obtained.

AuNPs with size distributions of $d = 34 \pm 3$ nm and 67 ± 4 nm were synthesized as follows. 0.8 mL of a 20 mM $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ aqueous solution, 80 μL of a 10 mM AgNO_3 , the colloidal Au seed solution, and water were mixed in a 50-mL glass vessel, where, the volume of the colloidal Au seed solution and water was 3.0 (0.6) mL and 34.0 (36.4) mL, respectively, for synthesis of the 34-nm (67-nm) AuNPs. Then, 6.0 mL of a 5.3 mM ascorbic acid solution was added to the mixed solution at a rate of 0.60 mL/min while stirring constantly. To complete the reaction, the stirring was continued for 30 min after finishing the addition of ascorbic acid solution. Finally, we obtained a colloidal solution of AuNPs with a diameter of 34 nm or 67 nm.

Alkanethiol capping of AuNPs was conducted according to our previous work [2].

Before thiolation, 10.0 mL of the colloidal solution of 14-nm AuNPs (Au seeds) was mixed with 27.9 mL of water and 6.0 mL of a 5.3 mM ascorbic acid solution to adjust the reaction condition. The colloidal solutions of 34-nm and 67-nm AuNPs were used as prepared. 10 mL of the colloidal AuNP solution was mixed with the thiol solution composed of 10.0 mL of acetone, 6.9 mg (24 μ mol) of 1-octadecanethiol (ODT) and 34.7 μ l (145 μ mol) of 1-dodecanethiol (DDT) in a polypropylene vessel. The molar ratio of ODT/DDT was 1:6. The mixed solution was stirred overnight at room temperature (RT) for exchange of the capping molecules. Then, obtained alkanethiol-capped AuNPs were extracted using hexane and methanol. A water-acetone/hexane interface was formed by adding 5.0 mL of hexane to the mixed solution, and alkanethiol-capped AuNPs concentrated at the interface. Subsequent addition of methanol to water-acetone phase promoted the concentration of AuNPs at the interface. The alkanethiol-capped AuNPs trapped at the interface were collected with a pipette and poured into a centrifuge tube. This extraction process was repeated until no AuNPs appeared at the interface. The extracted AuNPs were washed by three cycles of centrifugation at 6000 rcf for 10 min and redispersion into a mixture of acetone and hexane. The acetone/hexane ratio (v/v) was sequentially varied: 10:1, 1:1, and 1:9. After the final washing cycle, the supernatant was discarded, and then the alkanethiol-capped AuNPs were dried in an N₂ environment. We obtained a stable black powder, which can be kept in the N₂ environment.

References

- [1] Thuy, U. T. D.; Sakamoto, K.; Nishiyama, S.; Yanagida, S.; Liem, N. Q.; Miki, K., Assembly of Mid-Nanometer-Sized Gold Particles Capped with Mixed Alkanethiolate

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[2] Park, Y.-K.; Park, S., Directing Close-Packing of Midnanosized Gold Nanoparticles at a Water/Hexane Interface. *Chem. Mater.* **2008**, *20* (6), 2388-2393.

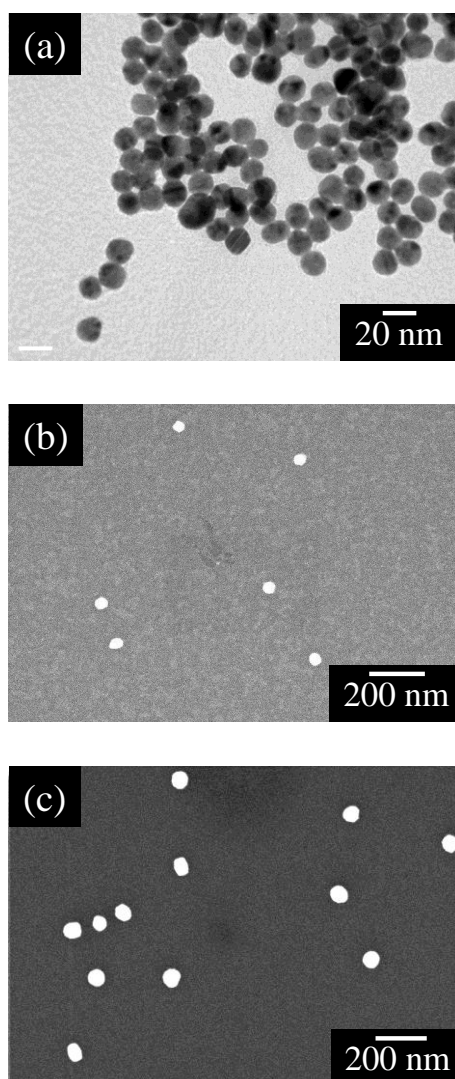


Figure S1. (a) TEM image of 14-nm AuNPs (Au seeds), and SEM images of AuNPs of (b) 34 nm and (c) 67 nm in diameter.

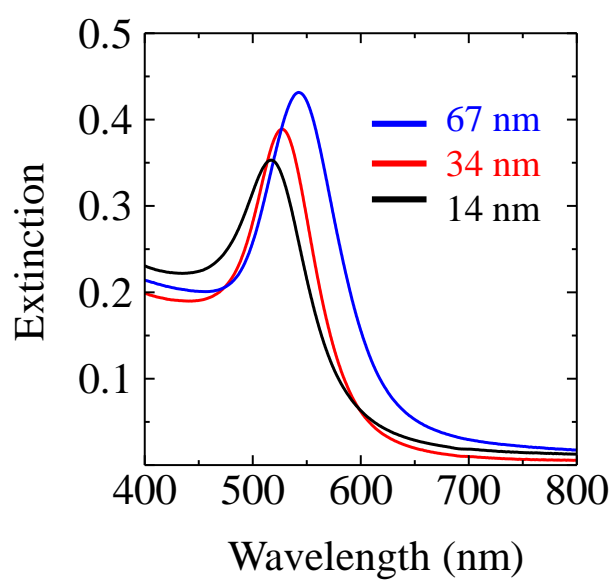
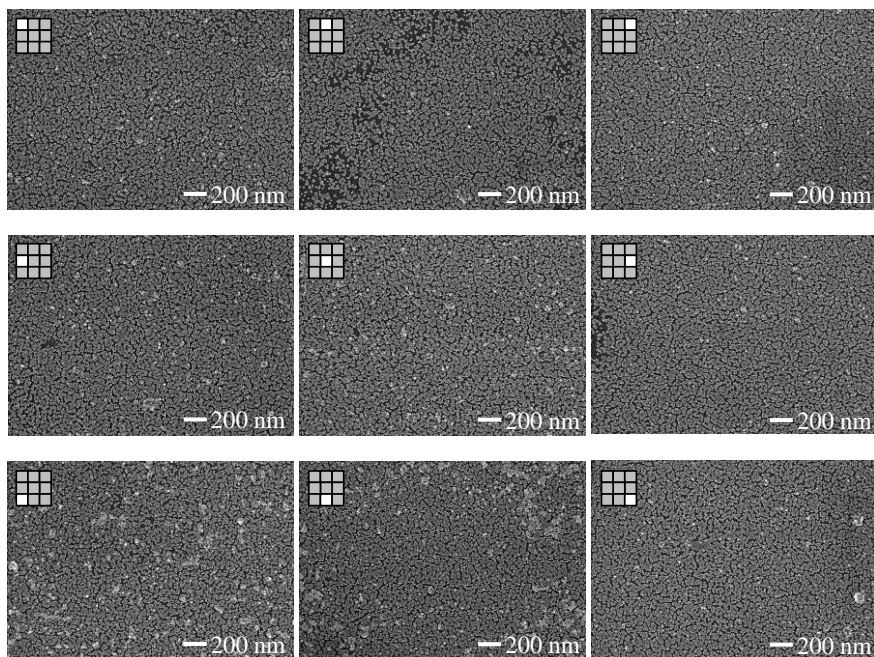


Figure S2. UV–vis extinction spectra of the as-prepared aqueous colloidal solutions of AuNPs with diameters of 14, 34, and 67 nm. To reduce the maximum absorbance, the solutions were diluted with water five-fold.

(a)



(b)

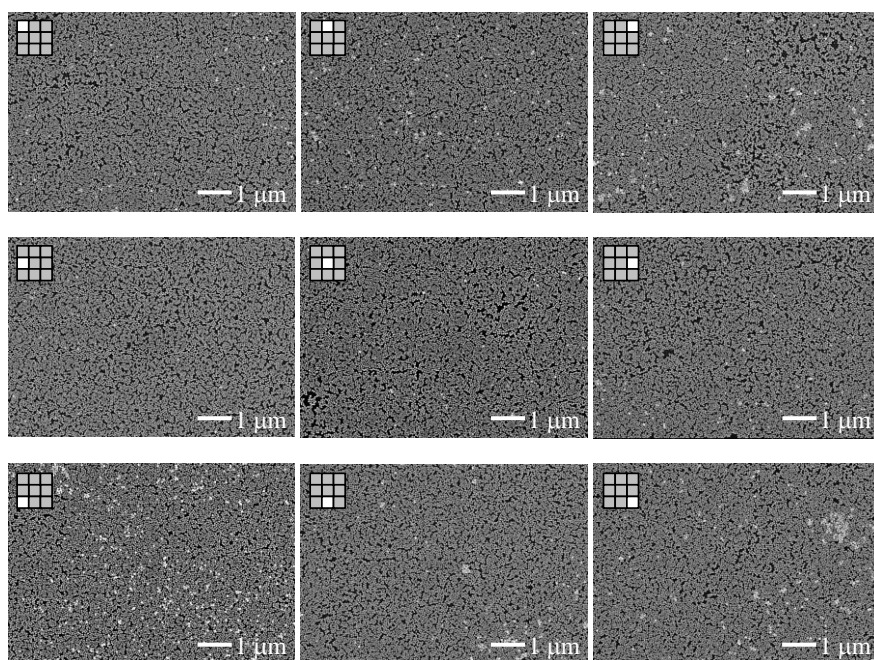


Figure S3. SEM images of the colloidal films of (a) 14 nm-AuNPs and (b) 67 nm-AuNPs taken at different positions, which are shown in the inset.

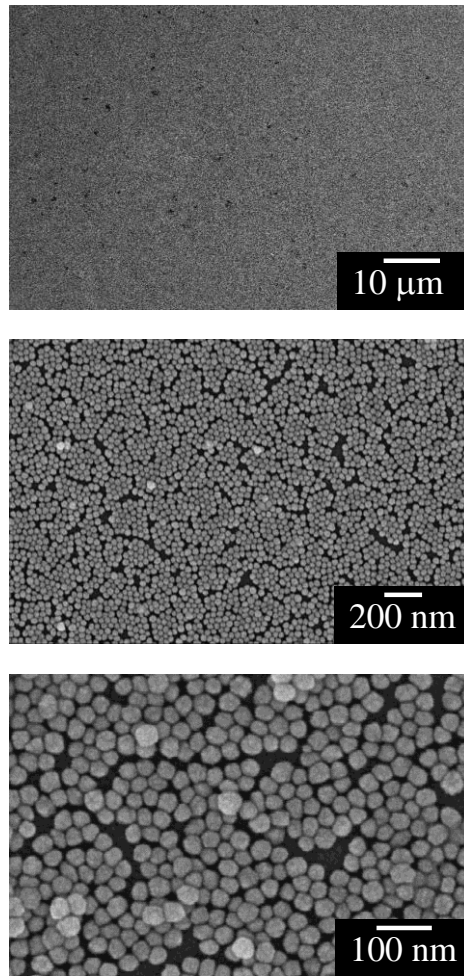


Figure S4. SEM images of the colloidal films of 33 nm-AuNPs formed on the 1.5-in. octagonal substrate. These images were acquired at magnifications of 1500×, 50000×, and 150000×.

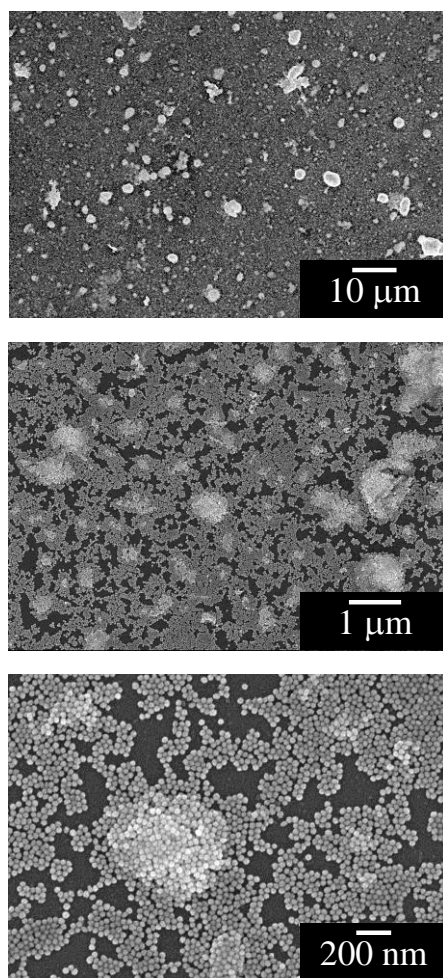


Figure S5. SEM images of the assembly of 34 nm-AuNPs after 5-minutes immersion without sonication 1. These images were acquired at magnifications of 1500×, 15000× and 50000×.