Electronic Supplementary Information (ESI)

Growth behavior of gold nanoparticles synthesized in unsaturated fatty acids by vacuum evaporation methods

Akito Fujita, Yusuke Matsumoto, Mitsuaki Takeuchi,* Hiromichi Ryuto and Gikan H. Takaoka

Photonics and Electronics Science and Engineering Center, Kyoto University, Kyoto 615-8510, Japan

Details of SAXS measurements and analysis

In SAXS measurements, the X-ray scattering from the holder and the solvent are included in the obtained profile and therefore are subtracted by the following equation.

$$I_0 = \frac{T_{holder}}{T_{sample}} I_{sample} - I_{holder}$$

I_0 is the scattering profile of the gold nanoparticles, I_{sample} is the scattering profile obtained from the whole sample, I_{holder} is the scattering profile obtained from the holder, T_{sample} is the transmission intensity of the whole sample and T_{holder} is the transmission intensity of the holder. The transmission intensity of the gold nanoparticles and the holder are obtained by irradiating the X-ray for 100 seconds. The transmission intensity were measured to evaluate the absolute scattering intensity of the sample and the holder. It is preferred to subtract the scattering profile by the solvent but in this experiment, the scattering intensity arising from the gold nanoparticles were too poor.

The transmission intensity obtained from the sample were sometimes lower than just the solvent. The main reason is the thickness of the copper plate merely verified from each holder. The holders were homemade and it was difficult to uniform the thickness of each holder precisely. Also, the concentration of the gold atoms (0.03 wt% or 1.9 mmol/dm^3 for our sample) were much lower than previous reports evaluating size distributions from SAXS measurements.[1,2] So, if the SAXS profiles obtained from the holder and the solvents are alike (if there are no characteristic peaks in the solvents scattering profile), subtracting the holder should be an adequate operation. Fig. S1(a) shows the scattering profile of the holder, the holder with ricinoleic acid and the holder with oleic acid and Fig. S1(b) shows the scattering profile of ricinoleic and oleic acid subtracted with the holder. There were no characteristic peaks shown in the solvents. Thus, we subtracted the scattering profile of the holder.

Scattering profiles of the sample, solvent and holder

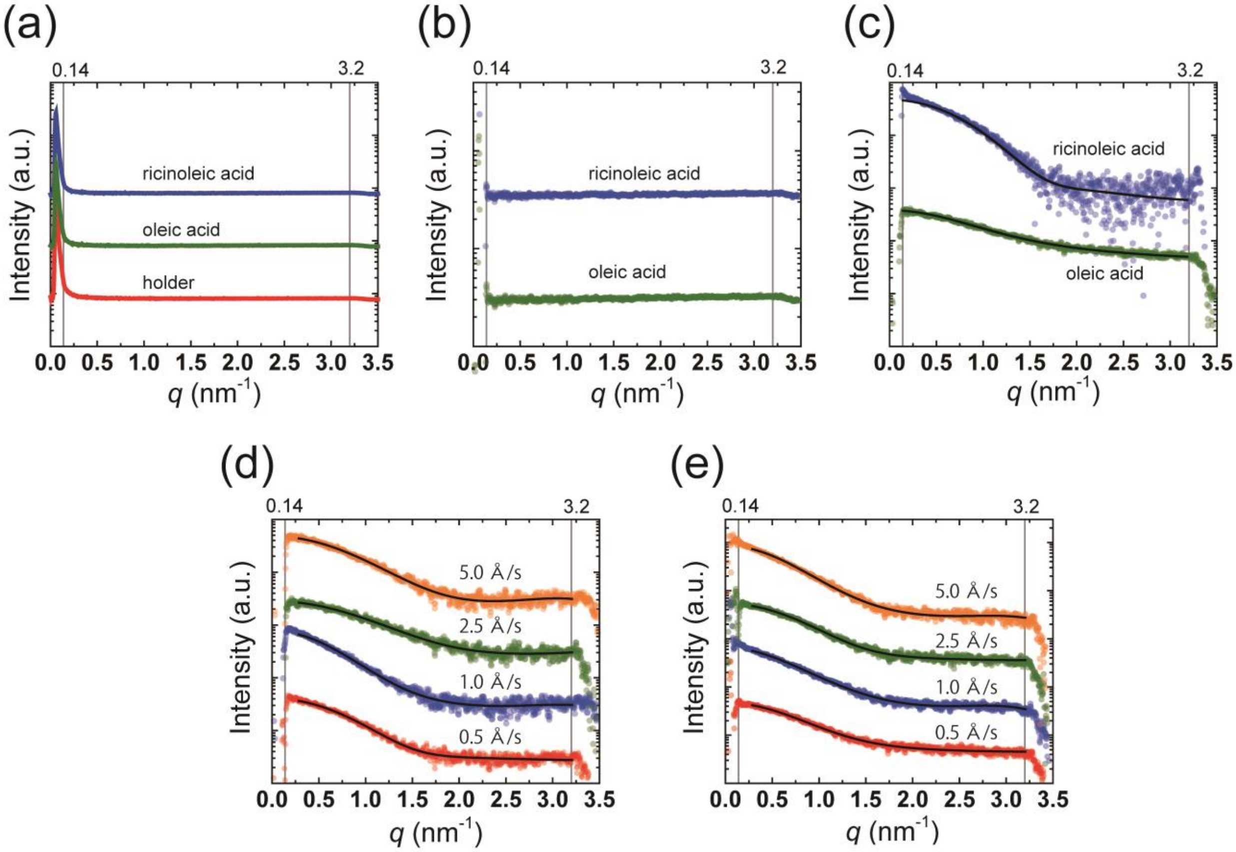
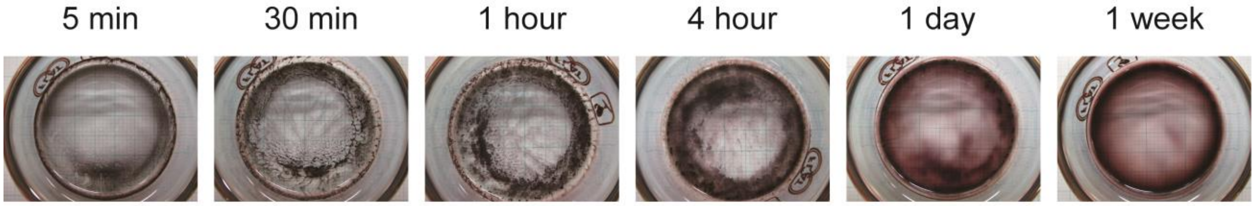


Fig. S1 (a) Scattering profiles of the holder, oleic acid and ricinoleic acid presented in red, green and blue lines, respectively. No characteristic peaks appeared in the holder and solvent. (b) Scattering profiles of ricinoleic and oleic acid shown in blue and green dots. The scattering profile of the holder was subtracted. Both scattering profiles were constant in the range of $0.14 < q < 3.2$ nm^{-1}, so using the holder as a reference should not affect the profile of the gold nanoparticles. (c) Scattering profiles of gold nanoparticles synthesized in ricinoleic and oleic acid shown in blue and green dots, respectively. The black lines are fitting curves. (d), (e) Scattering profiles of gold nanoparticles synthesized in ricinoleic and oleic acid, respectively. The black lines are fitting curves. The deposition rate were changed from 0.5 Å/s to 5.0 Å/s. In all profiles, the plots are multiplied by 10, 100 or 1000 to avoid the overlap of the plots.

Visual observation of the gold nanoparticle synthesis


(a) Ricinoleic acid

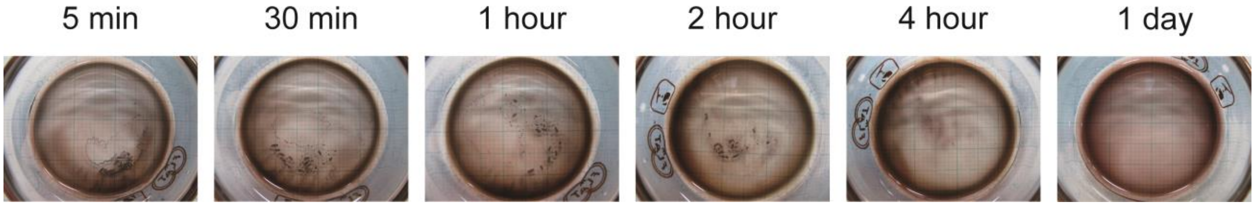

(b) Oleic acid

Fig. S2 Photographs of the sample after deposition as a function of time of (a) ricinoleic acid and (b) oleic acid. In ricinoleic acid, black aggregates continuously emerge until 1 hour. After 4 hours, the aggregates start to blur and the solvent slowly turns dark red indicating the formation of nanoparticles. It takes about a week to obtain a homogenous dark red color for the whole solvent. In oleic acid, black aggregates are formed on the surface and the solvent partially turns brown. The aggregates shrink with time and can’t be confirmed 4 hours after deposition. After 1 day, a homogenous color is obtained and the color changed from brown to a slight red-brown color.

Observation of lattice planes in oleic acids

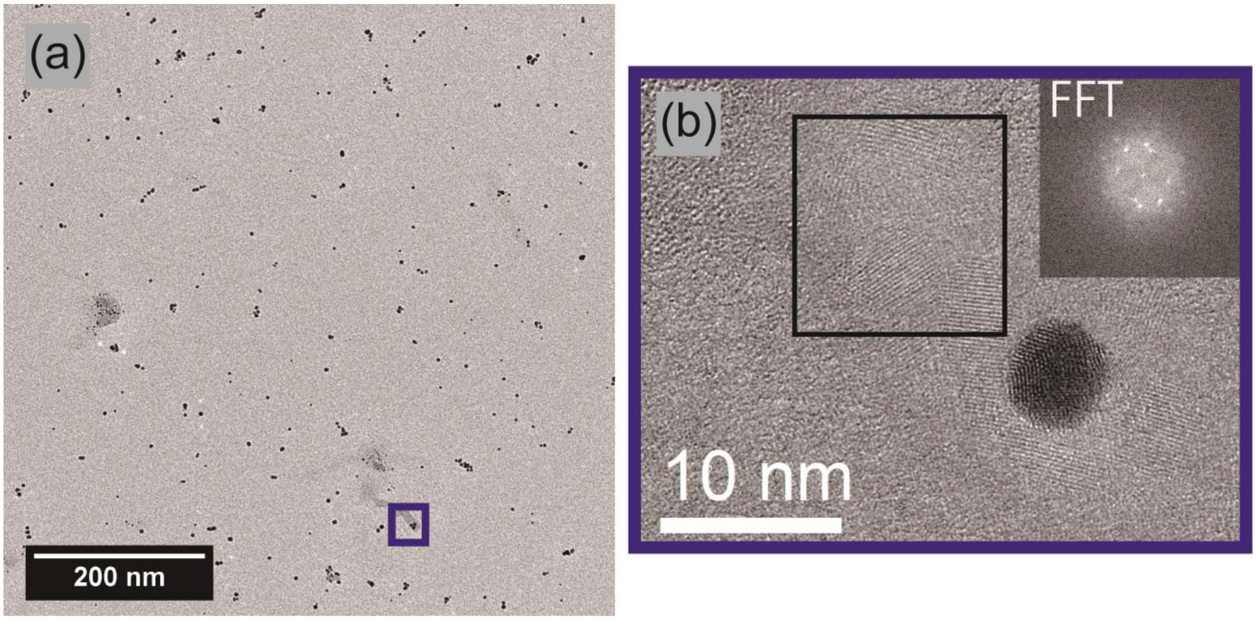


Fig. S3 TEM images of oleic acid. The magnification of the original TEM images were (a) 30k and (b) 300k. TEM images (a) and (b) were taken 10 minutes after deposition. In the TEM image (a), the nanoparticles were well dispersed and a contrast darker than the background can be recognized around some nanoparticles inside the blue square. (b) is the magnified view of the blue square shown in (a). Nanoparticles are observed and striped patterns can be seen around them. The inset in (b) stands for the fast Fourier transform (FFT) of the black square. Diffraction points can be seen from the FFT and therefore, the striped patterns are crystalline films, probably about a few monolayers. These films have also been observed in ricinoleic acid and should be residues of the aggregates formed on the surface of the solvent.

The influence of gas exposure to the samples

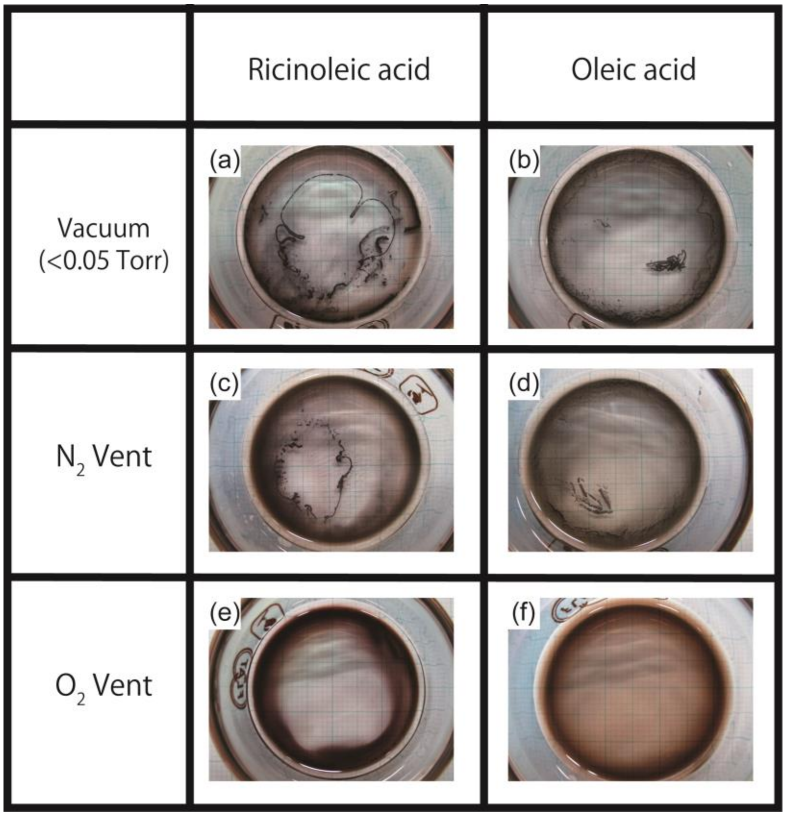


Fig. S5 Visual observations of the influence of gas or vacuum exposure to the samples. Control experiments were conducted as follows. After the deposition, each solvent was aged under 3 different atmosphere for a day: (a), (b) vacuum under 0.05 Torr, (c), (d) 1 atm nitrogen gas for and (e), (f) 1 atm oxygen gas mixed with helium (O_2 : He = 7:3). The samples were taken out the next day. The vacuum was never broken during the experiment until the samples were taken out. Black aggregates remained when left in vacuum and vented with nitrogen for both solvents. However, the aggregates disappeared when the apparatus was vented with the oxygen mixed gas. Considering helium is an inert gas, the oxygen should have triggered the phenomenon.

XPS spectra of gold nanoparticles

XPS measurements were conducted by a Shimadzu Kratos AXIS-ULTRA DLD apparatus equipped with an Al Kα source. Samples were prepared by functionalizing Si substrates with 3-mercaptopropyltrimethoxysilane (MPTMS, purchased from Shin-Etsu Chemical Co., Ltd.). The substrates were immersed in a hot 5 mM toluene solution of MPTMS for 40 minutes. Then, the substrates were immersed in the solvents containing nanoparticles for several days to immobilize the nanoparticles on the substrate. Finally, the substrates were washed with 2-propanol and dried with N_2 flow. The spectra were calibrated by the C 1s peak (284.6 eV). The peak area of the Au $4f_{7/2}$ and $4f_{5/2}$ were fixed to 4 : 3.

The XPS spectra for Au 4f and S 2p are shown in Fig. S6 and S7, respectively. The XPS spectra of Au 4f for the gold nanoparticles showed 2 peaks around 84.0 eV and 87.7 eV, which represent Au $4f_{7/2}$ and Au $4f_{5/2}$ peaks in bulk gold.[3,4] Additional peaks of the spectra with a positive shift of 0.8 eV from the bulk gold peaks were found, which should be assigned to the Au-S bond, induced by the mercapto group in the MPTMS. When gold nanoparticles are oxidized, the surface turns into Au_2O_3 where the Au 4f shows a positive shift of about 1.8 eV.[4] We would also like to mention that prior XPS research on gold nanoparticles immobilized by thiol monolayers showed small positive 1.7 eV shift peaks, which they concluded to partial charging in the sample.[5] We can't decide from the spectra whether the peaks arise from oxidized gold atoms or charging. However, even if we suppose the peak arises from oxidation, it is less than 5% of the overall Au signal. Thus, we can conclude that the oxidation of gold nanoparticles are negligible and can't be the major factor inducing the change from aggregate to nanoparticle or thin film to nanoparticle.

The S 2p spectra show 3 peaks. The broad peak around 168 eV arises from the oxidation of sulfer.[6] The peak appears in self assembled monolayers (SAMs) as in this experiment, where the

SAMs are exposed to the air. 2 peaks at 164.0 eV and 162.8 eV are also recognized. The 164.0 eV peak represents from reduced sulfur (S-H bond) and the 162.8 eV peak arises from the Au-S bond,[6] which is consistent with the Au 4f spectra. The peak values differ from prior research because the S 2p signals are poor.

The O 1s signals also show 3 peaks. The main peak around 532 eV represents the siloxane bond formed between the MPTMS and the silicon substrate.[7] This was evidenced since the same peak was found in MPTMS monolayers without immobilizing gold nanoparticles. The 533.2 eV peak represents the naturally oxidized SiO_2 surface[8] and the 531.3 eV peak represents the carboxyl group of the UFAs.[9] Also, the O 1s peak in Au_2O_3 has a peak around 530 eV,[10] which is out of the range in this spectra. Therefore we can't see evidence of oxidation in the O 1s spectra.

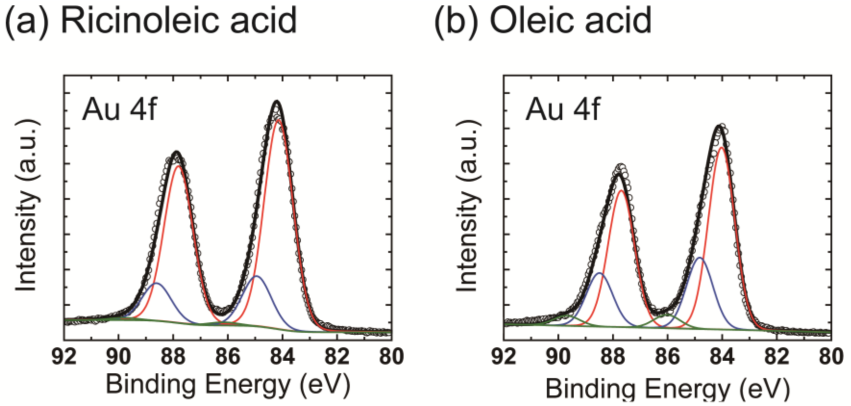


Fig S6 XPS spectra of Au 4f measured from gold nanoparticles synthesized in (a) ricinoleic acid and (b) oleic acid. The red and blue peaks are assigned for bulk gold and Au-S bonds, respectively. The green peak occurs from partially charged particles or oxidized gold atoms.

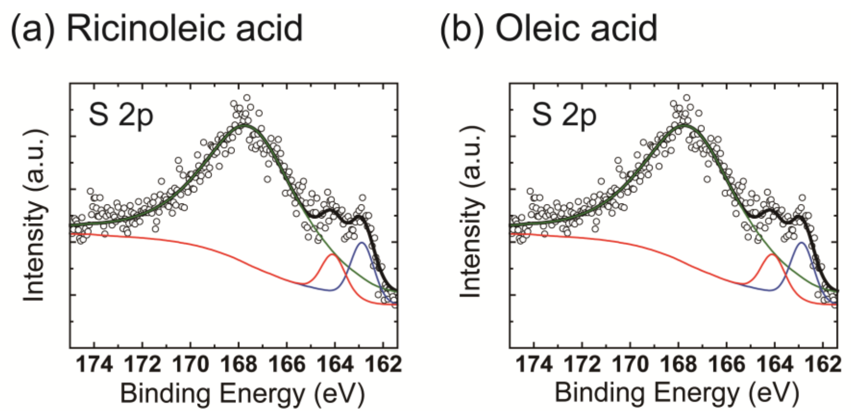


Fig. S7 XPS spectra of S 2p measured from gold nanoparticles synthesized in (a) ricinoleic acid and (b) oleic acid. The green, red and blue peaks arise from oxidized sulfur, reduced sulfur and Au-S bonds, respectively.

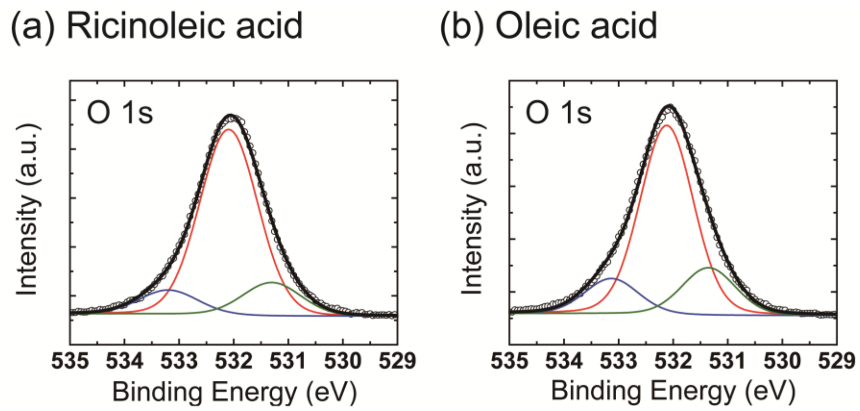


Fig. S8 XPS spectra of O 1s measured from gold nanoparticles synthesized in (a) ricinoleic acid and (b) oleic acid. The red, blue and green peaks arise from Si-O-Si bonds, SiO_2 and COOH, respectively.

Reference

1 Y. Hatakeyama, M. Okamoto, T. Torimoto, S. Kuwabata and K. Nishikawa, *J. Phys. Chem. C*, 2009, **113**, 3917-3922.

2 H. Wender, R. V. Goncalves, A. F. Feil, P. Migowski, F. S. Poletto, A. R. Pohlmann, J. Duopnt and S. R. Teixeira, *J. Phys. Chem. C*, 2011, **115**, 16362-16367.

3 M. Hirano, K. Enokida, K. Okazaki, S. Kuwabata, H. Yoshida and T. Torimoto, *Phys. Chem. Chem. Phys.*, 2013, **15**, 7286-7294.

4 L. K. Ono and B. R. Cuenya, *J. Phys. Chem. C*, 2008, **112**, 4676-4686.

5 Y. Joseph, I. Besnard, M. Rosenberger, B. Guse, H.-G. Nothofer, J. M. Wessels, U. Wild, A. Knop-Gericke, D. Su, R. Schlögl, A. Yasuda and T. Vossmeyer, *J. Phys. Chem. B* 2003, **107**, 7406-7413.

6 J. Singh and J. E. Whitten, *J. Phys. Chem. C*, 2008, **112**, 19088-19096.

7 L. Junyan, H. Ling, L. Weidong and L. Hongjie, *Polym. Int.*, 2009, **58**, 1283-1290.

8 Z. Li and Y. Zhu, *Appl. Surf. Sci.*, 2003, **211**, 315-320.

9 S.-Y. Lee and M. T. Harris, *J. Colloid Interface Sci.*, 2005, **293**, 401-408.

10 D. C. Lim, I. Lopze-Salido, R. Dietsche, M. Bubek and Y. D. Kim, *Chem. Phys.*, 2006, **330**, 441-448.