Electronic Supplementary Material (ESI) for Nanoscale.

Supporting information for:

Vertical Segregation in the Self-assembly of Nanoparticles at Liquid/Air Interface

Yanming Liu,[§] Yang Liu,[§] Peng Tao, Wen Shang, Chengyi Song* and Tao Deng*

State Key Laboratory of Metal Matrix Composites, School of Materials Science and Engineering, Shanghai Jiao Tong University, 800 Dong Chuan Road, Shanghai 200240, P.R.China.

[§]Y.M.Liu and Y. Liu contributed equally to this work.

Corresponding author: dengtao@sjtu.edu.cn; chengyi2013@sjtu.edu.cn

Table of Contents

1. Materials and Instrumentations
2. Preparation of metallic colloidal nanoparticles (NPs)
3. Preparation of size-segregated double-layer NP film
4. Energy trap of trapped NPs at water/air interface
5. Supplementary data (Figures S1-S13)
6. References

1. Materials and Instrumentations

All chemicals were obtained from commercial sources and used without further purification. Transmission electron microscopy (TEM) samples were prepared by pipetting one drop of solution onto a 3-mm-diameter copper grid coated with carbon film. The excess solution was removed from grid with a piece of filter paper. TEM was conducted on a JEOL JEM-2010 instrument operated at 200 kV and the images were collected using a Gatan CCD image system. Scanning electron microscopy (SEM) samples were prepared by transferring Au thin films onto clean Si wafers. The Si-wafers was modified with fluorosilane using methods reported in the literature.[1] The Si wafers were firstly washed by acetone, ethanol, and distilled water, respectively, in ultrasonic bath for 10 mins. After drying in air completely, the wafers would be further cleaned in the Plasmon Cleaning (PDC-32G, HARRICK PLASMA) to remove trace amount of organic impurities and rinsed thoroughly. Next, the as-cleaned Si wafers were placed in a desiccator filled with 1H, 1H, 2H, 2H-perfluorooctyltrichlorosilane (97%, Alfa Aesar) vapor under a negative pressure for about 50 mins, which was aimed to make Si wafers surface hydrophobic. SEM instrument (Quanta 250 from FEI, 20 kV) equipped with energy dispersive spectroscopy (EDS) (Oxford Instruments, 80 mm^2 detector). UV-Vis Spectra were collected on UV-Vis spectrometer (Ocean Optics, Model: HR2000+CG). Zeta potential was measured on a Zeta sizer-nano series instruments (Malvern instruments LTD).

2. Preparation of metallic colloidal NPs

Synthesis of 10-nm, 30-nm, 50-nm and 100-nm colloidal gold (Au)NPs:[2]

Citrate stabilized 10-nm colloidal Au NPs: Solution of 38.8 mM trisodium citrate dihydrate (99%, Aladin) was made by directly dissolving sodium citrate powder in DI water (NANOpure, Millipore Water Purification System; 18.2 MΩ). Aqueous solution of 1 mM tetrachloroauric acid ($HAuCl_4$) was prepared by dissolving tetrachloroauric acid (49~50% Au basis; Aladin) in water. In a 100-mL round-bottom flask attached with a condenser, 50 mL of the $HAuCl_4$ aqueous solution was brought to boiling with vigorous stirring. After the addition of 5 mL of 38.8 mM sodium citrate to the above solution, the color of the solution changed from pale yellow to deep red. The mixture was boiled for 15 minutes and stirred for additional 1 hour until the solution cooled down.

Citrate stabilized 30-nm, 50-nm, 100-nm colloidal Au NPs: Large colloidal Au NPs were synthesized by stepwise NH_2OH-seeding method (see ref.2 for synthetic details). Citrate capped 10-nm colloidal Au NP were used as seeds to prepare 30-nm, 50-nm and 100-nm colloidal Au NP. Stock solutions of 1% $HAuCl_4$ and 0.294 MNH_2OH aqueous solution were utilized as Au source and reducing reagent, respectively.

Synthesis of concentrated 50-nm, 100-nm colloidal Au NPs: As-synthesized 50-nm colloidal Au NPs solution was heated under sonication until most of solvent was evaporated away. Concentrated 100-nm Au NP solution was prepared by the following method. The newly made 100-nm colloidal Au NP solution was left undisturbed for two weeks. Due to nature sedimentation, 100-nm particles precipitated at the bottom. The precipitates were collected and re-dispersed in DI water. Concentrated colloidal Au NP solutions were stored at room temperature for future use. All the experiments in this report used concentrated 50-nm, 100-nm colloidal Au NP solutions for the assembly studies.

Concentration of the as-synthesized 10-nm, 30-nm, concentrated 50-nm andconcentrated100-nm colloidal Au NPs (Based on the materials we use):

1) Concentration of 10-nm Au NPs (aq): 1.11×10^{13}/mL

2) Concentration of 30-nm Au NPs (aq): 1.11×10^{12}/mL

3) Concentration of 50-nm Au NPs (aq): 1.46×10^{11}/mL

4) Concentration of 100-nm Au NPs (aq): 1.82×10^{10}/mL

Concentration of concentrated 50-nm and 100-nm particles are further determined by UV-Vis spectroscopy (Figure S3): the concentration of concentrated 50-nm NPs is ~ $2.16\times1.46\times10^{11}$/mL=$3.15\times10^{11}$/mL; the concentration of concentrated 100-nm NPs is ~ $8.54\times1.82\times10^{10}$/mL=$1.55\times10^{11}$/mL.

Synthesis of 90-nmcolloidal silver (Ag) NPs:

Ag NPs were synthesized by following the published method.[3] Aqueous solution of 0.02% $AgNO_3$ was prepared by dissolving 27 mg $AgNO_3$(s) in 250-mL round flask with 150-mL DI water. After the solution was brought to boiling, 3 mL of 1% fresh prepared sodium citrate solution was added while stirring vigorously. The color changed from light yellow to opaque gray, suggesting the formation of individual NPs. After the solution was boiled for 45 min, it was cooled to room temperature. As-synthesized Ag NP solution was centrifugated (7000 rpm for 2 min) and then half of the supernatant was discarded. The pellet of the product was re-dispersed in the remaining mother solution. Concentrated colloidal Ag NP solution was stored at 4°C for future use.

3. Preparation of size-segregated double-layer NP film

10-nm/100-nmAu NP layered structures: 3mL of freshly prepared 10-nm colloidal Au NP solution was mixed with 2 mL of 100-nm colloidal Au NP solution and 1 mL of DI water in a 25-mL beaker (The concentration of 100-nm NPs in the mixture was $\frac{2\,mL}{6\,mL}\times1.55\times10^{11}$/mL =$5.17\times10^{10}$/mL; the concentration of 10-nm NPs in the mixture was $\frac{3\,mL}{6\,mL}\times1.11\times10^{13}$/mL =$5.55\times10^{12}$/mL). The above mixture was vortexed for a few seconds. The beakers together with small petri dish filled with formic acid were placed inside a vasline sealed desiccator and then left undisturbed at room temperature. The solution gradually turned colorless and a shinny thin film of Au NPs floating at water/air interface was observed after one day.

Note: 50-nm/100-nm Au NP layered structures were prepared in a similar fashion, except the solution was composed with 3 mL of 50-nm Au NP (aq), 2.5 mL of 100-nm Au NP (aq), and 0.5 mL of water.

Note: 30-nm Au NP/90-nm Ag NP layered structures were prepared in a similar fashion, except 4mL of 30-nm Au NP (aq), and 2mL90-nm Ag NP(aq) were used in the assembly.

Control experiment of the drop-cast samples: A drop of the same solution used in the assembly of 10-nm/ 100-nm Au NP layered structures was placed on a cleaned Si wafer and let dry in air overnight.

4. Energy trap of trapped NPs at water/air interface

The calculations of the energy traps are shown as follows:

$$E_{trap} = \Delta E_{particle} + \Delta E_{interface} = \{\gamma_{water/particle}[4\pi R^2 - 2\pi R^2(1 + co$$

$$[2\pi R^2(1 - cos\theta)]\} + \gamma_{air/water}(\pi R^2 sin^2\theta)$$

In the calculation, $\mathbf{E_{trap}}$ is the overall energy needed (energy trap) to move the particle back from interface to water, **R** is the radius of the particle, $\boldsymbol{\gamma}_{\mathbf{water/particle}}$ is the interfacial surface tension between water and particle surface, $\boldsymbol{\gamma}_{\mathbf{air/particle}}$ is the interfacial surface tension between air and particle surface, $\boldsymbol{\gamma}_{\mathbf{air/water}}$ is the interfacial surface tension between air and water, and **θ** is the contact angle of water at the particle surface.

With the balance of interface forces at the three phase contact line:
$\gamma_{air/particle} = \gamma_{water/particle} + \gamma_{air/water} cos\theta$

So $E_{trap} = \gamma_{air/water} \pi R^2 (1 - cos\theta)^2$

The key point is to determine the contact angle of individual nanoparticles at the water/air interface. Based on the classic Wenzel equation:[4]

$$\cos\theta^* = r\cos\theta$$

where θ^* is apparent contact angle which corresponds to the contact angle measured on the assembled film; **r** is roughness ratio for the films of nanoparticles, which is larger than 1; θ is intrinsic contact angle that corresponds to the contact angle of individual nanoparticles. The contact angle θ of individual nanoparticles at the water/air interface depends on the apparent contact angle θ^* of assembled nanoparticle film. So we measured the contact angle on the as assembled films of 10-

nm, 50-nm, and 100-nm particles (Figure S13) and concluded that the contact angle of the individual particles at the three phase contact line should be close to 90°.

If θ is chosen as 90°, the energy traps for the particles with diameter of 10 nm and 100 nm are ($\gamma_{\mathbf{air/water}}$ = 72mNm^{-1}):

$\mathbf{E_{trap}}$ (θ=90°, R=5 nm) $= 5.66 \times 10^{-18}$J

$\mathbf{E_{trap}}$ (θ=90°, R=50 nm) = 5.66×10^{-16}J

For the thermal energy that was the major driving force to detach the particles from the interface:

$E_{thermal} = k_BT = 1.3806488(13) \times 10^{-23}\,(J/K) \times 298(K) = 4.11 \times 10^{-21}\,J$

(k_B is the Boltzmann constant, T is the thermodynamic temperature.)

So

$\mathbf{E_{trap}}$ (θ=90°, R=5 nm) ~ 1.37×10^3 K_BT

$\mathbf{E_{trap}}$ (θ=90°, R=50 nm) ~ 1.37×10^5 K_BT

Such a large energy trap makes the trapped particles very stable at the water/air interface. Due to the electrostatic repulsion and the dipole-dipole interaction, the trapped NPs can interact with neighbouring NPs and form a film at the air-water interface.

5. Supplementary Data (Figures S1-S13)

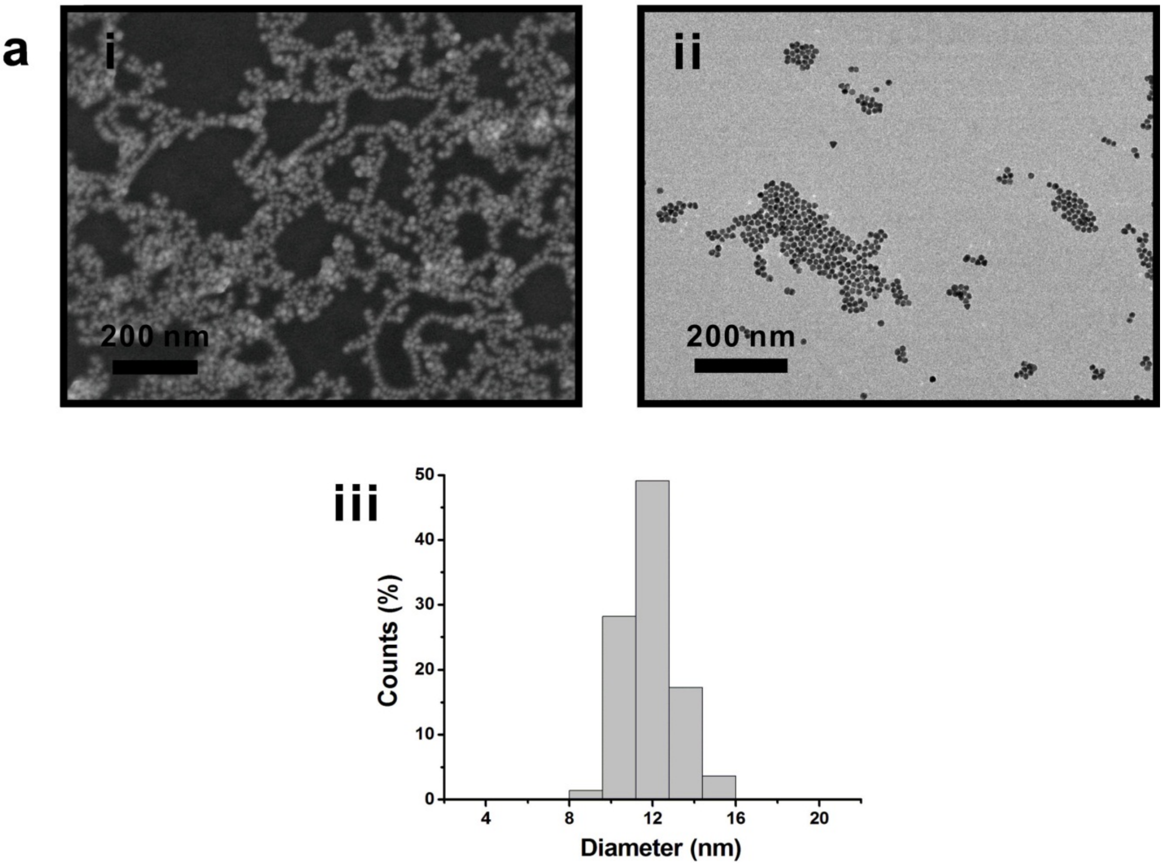


Figure S1a. (i) SEM and (ii) TEM images of 10-nm Au NPs obtained via published method.[2] (iii) Size distribution of Au NPs (based on 219 counts; NP diameter = 12.0 ± 1.2 nm).

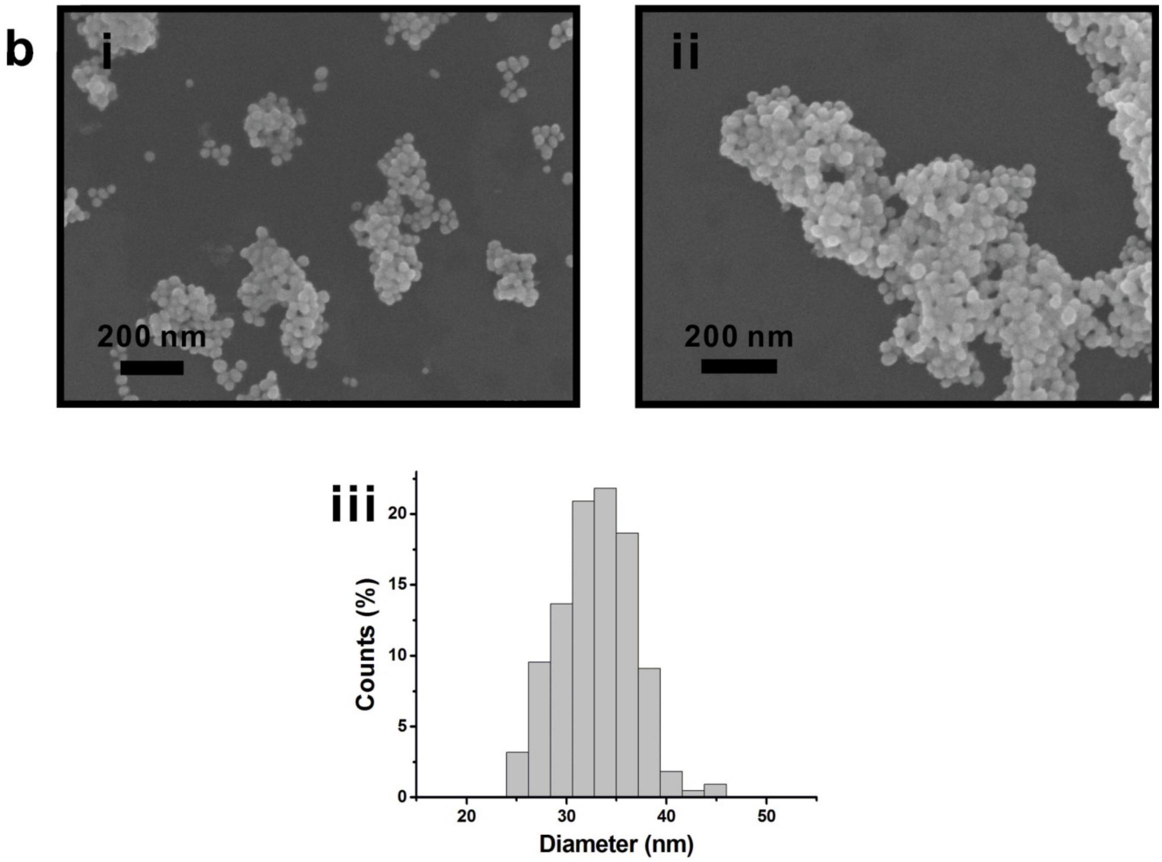


Figure S1b. (i-ii) SEM images of 30-nm Au NPs obtained via published method.[2] (iii) Size distribution of Au NPs (based on 220 counts; NP diameter = 33.0 ± 3.8 nm).

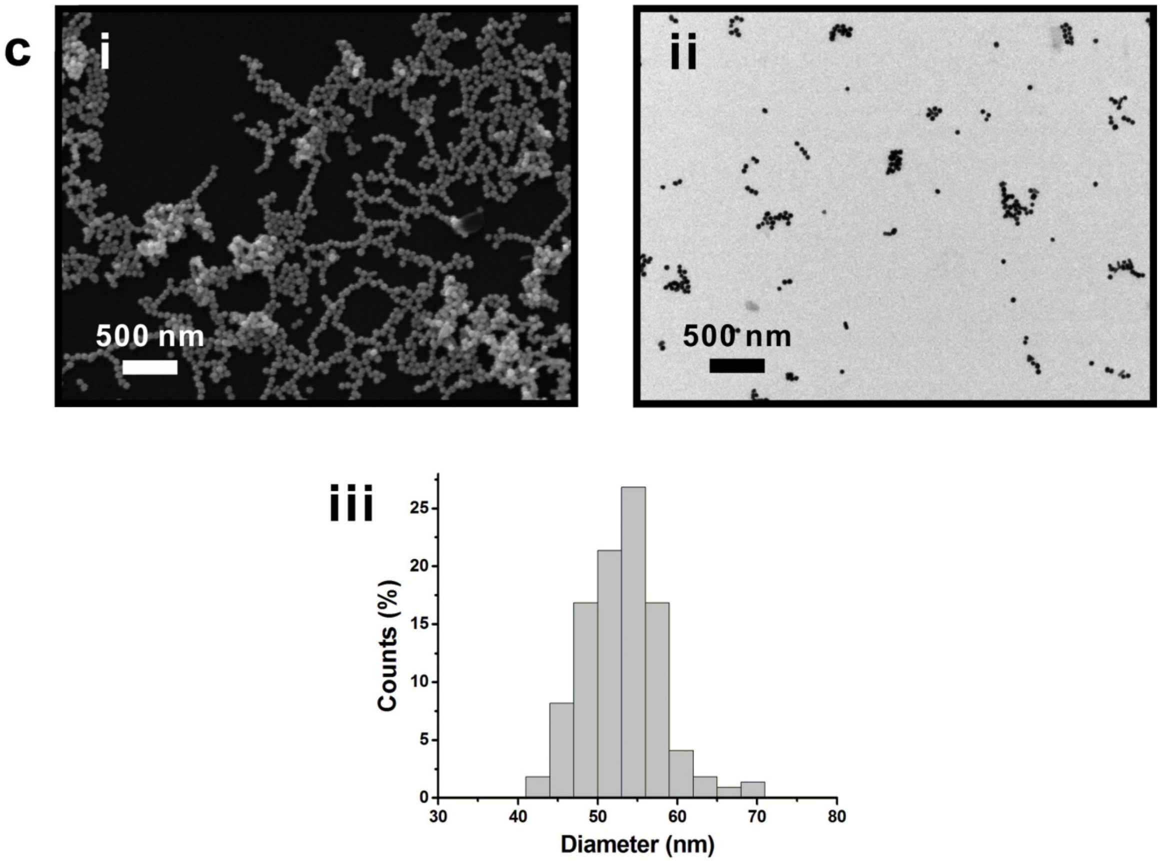


Figure S1c. (i) SEM and (ii) TEM images of 50-nm Au NPs obtained via published method.[2] (iii) Size distribution of Au NPs (based on 219 counts; NP diameter = 53.1 ± 4.8 nm).

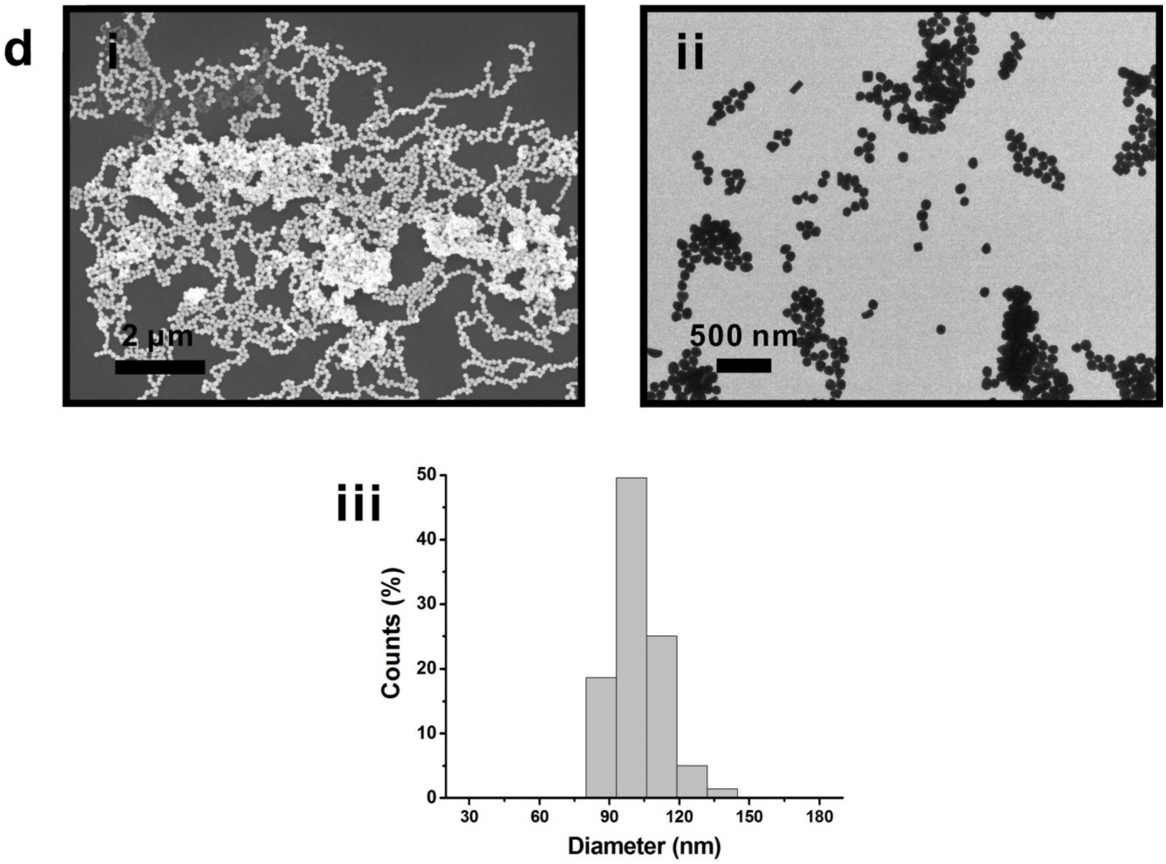


Figure S1d. (i) SEM and (ii) TEM images of 100-nm Au NPs obtained via published method.[2] (iii) Size distribution of Au NPs (based on 220 counts; NP diameter = 101.8 ± 10.9 nm).

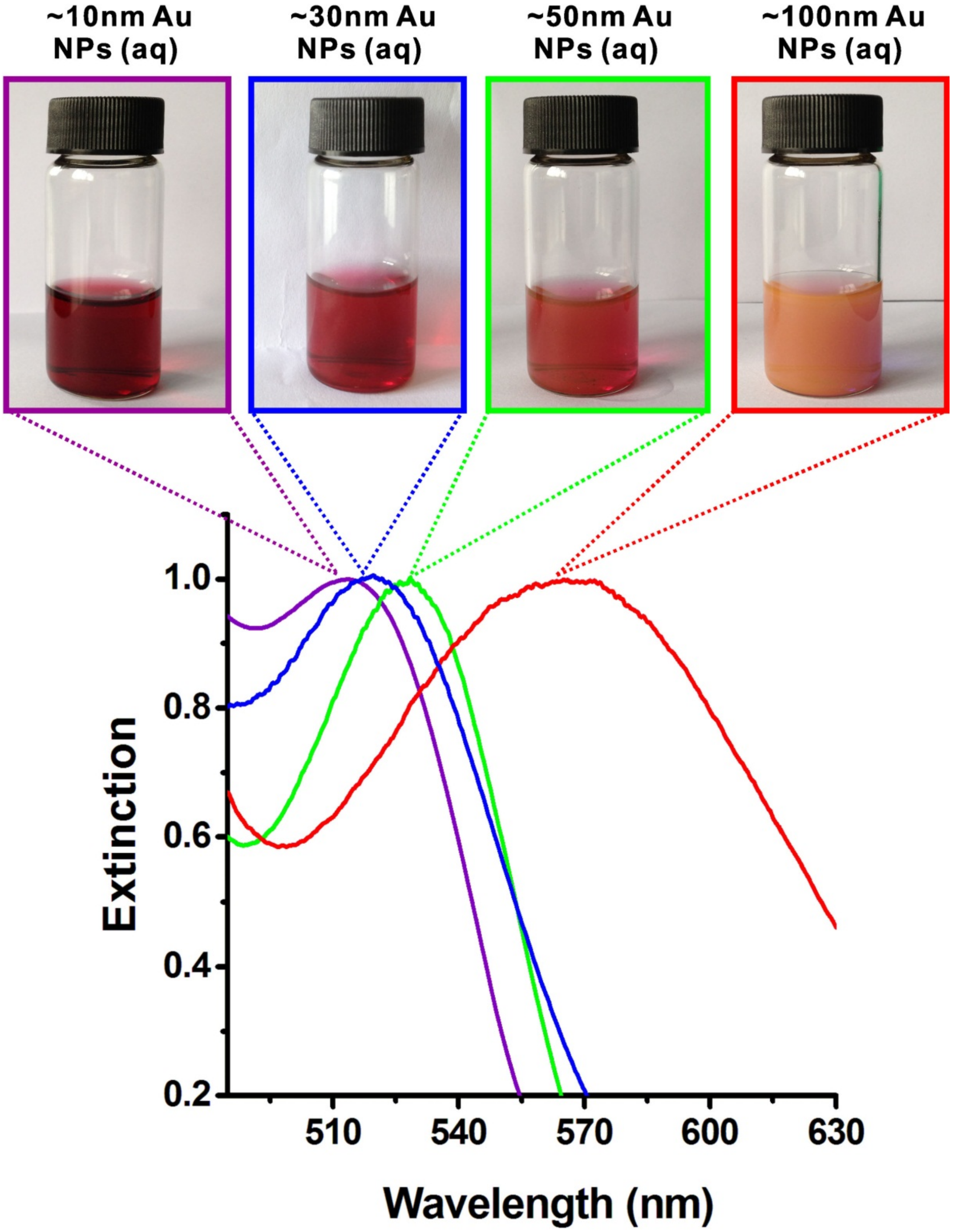


Figure S2. The UV-Vis spectra of the solutions of ~10, ~30, ~50, and ~100 nm Au NPs synthesized in this work. The absorbance maximums are observed at 513 nm, 520 nm, 528 nm and 575 nm, correspondingly. The peaks are significantly red-shifted and broadened as the size increases, consistent with what reported in the literature.[5, 6]

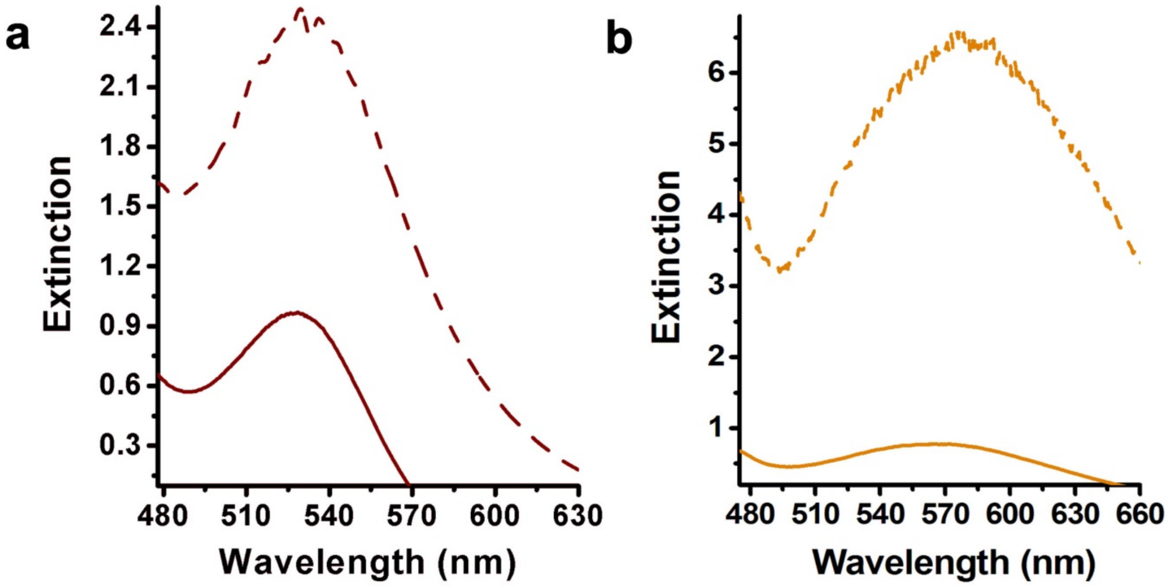


Figure S3. The UV-Vis spectra of 50-nm and 100-nm colloidal Au NPs before (solid lines) and after concentration (dotted lines). (Extinction of 50-nm Au NP solution at 528 nmare1.20 (before) and 2.589 (after); Extinction of 100-nm Au NP solution at 575 nm are 0.767 (before) and 6.55 (after).

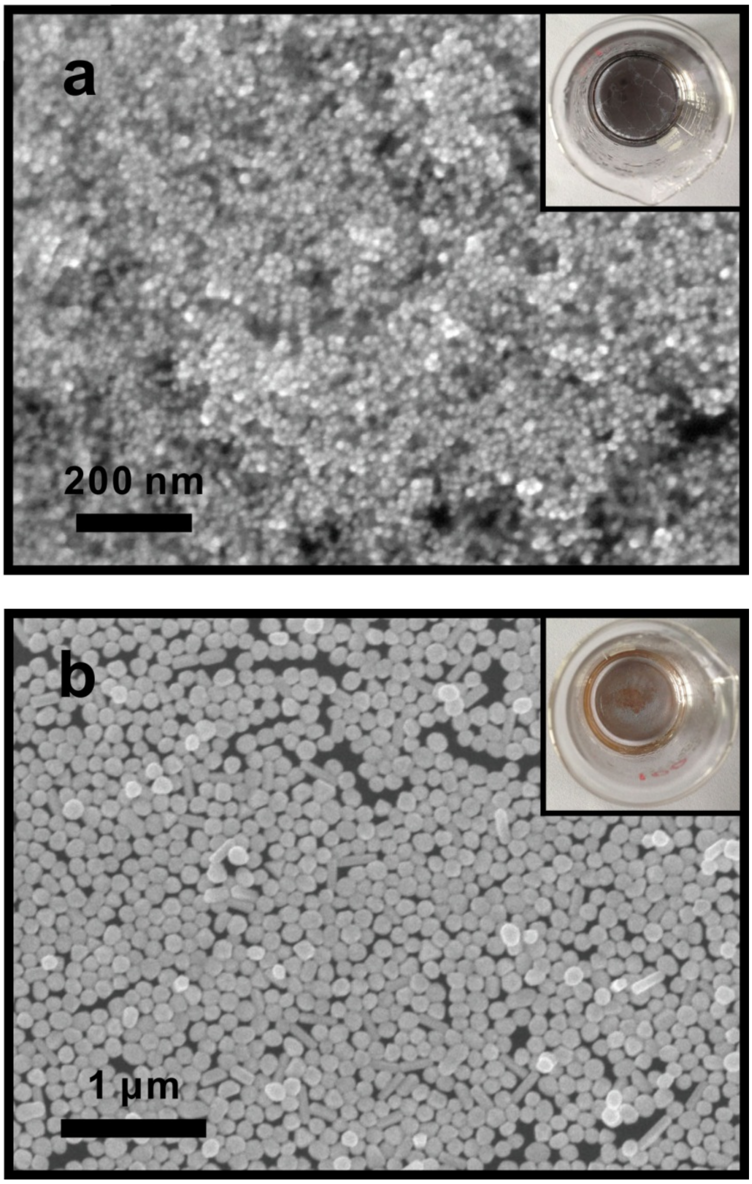


Figure S4. (a) SEM image of 10-nm Au NP film formed at water/air interface after incubating in the presence of formic acid vapor for one day. (b) SEM image of 100-nm Au NP film formed at water/air interface after incubating with formic acid vapor for one day. The inset pictures are optical images of the films.

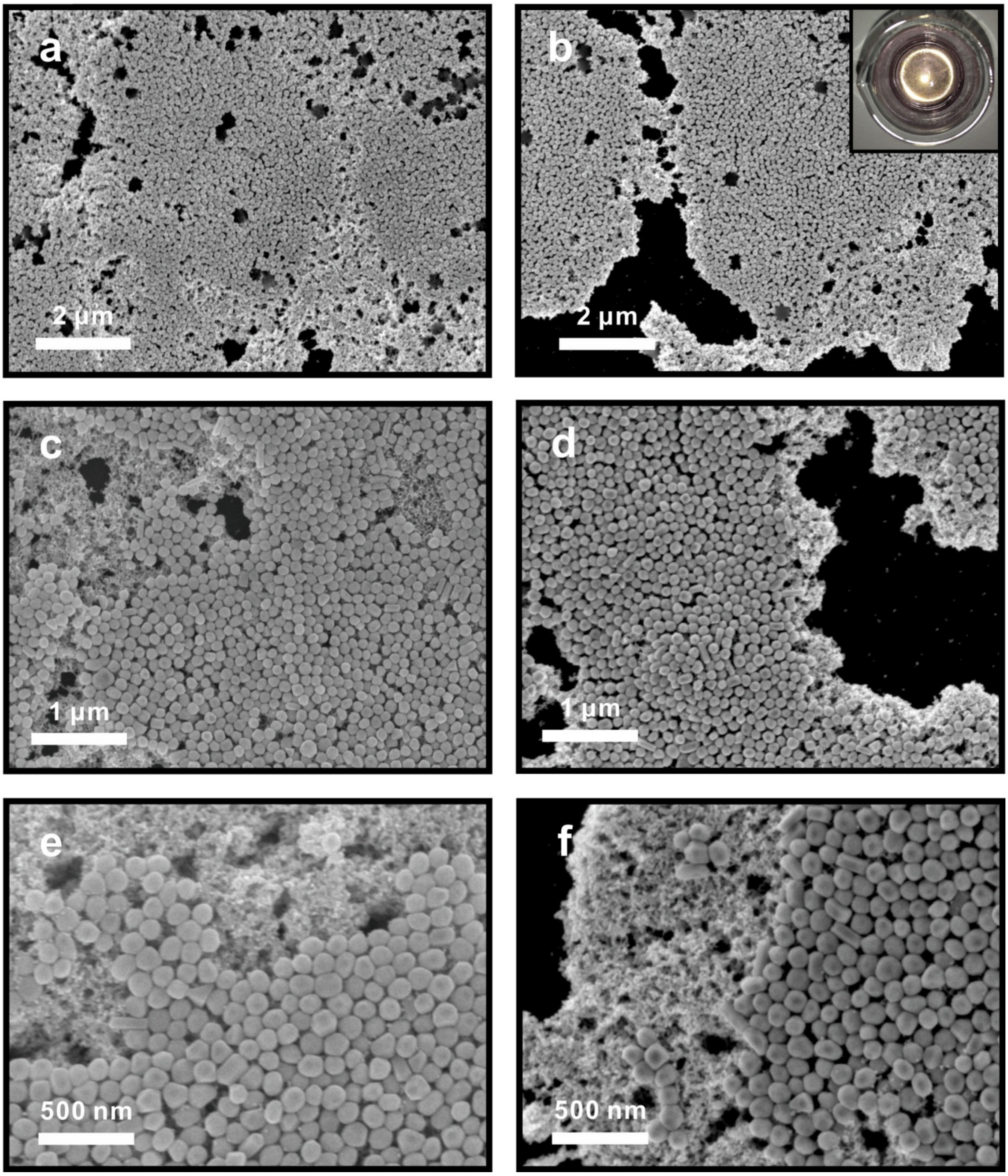


Figure S5. Additional SEM images (a-f) of 10-nm/100-nm size-segregated Au NP films with the layer of 100-nm NPs on top of the layer of 10-nm NPs.

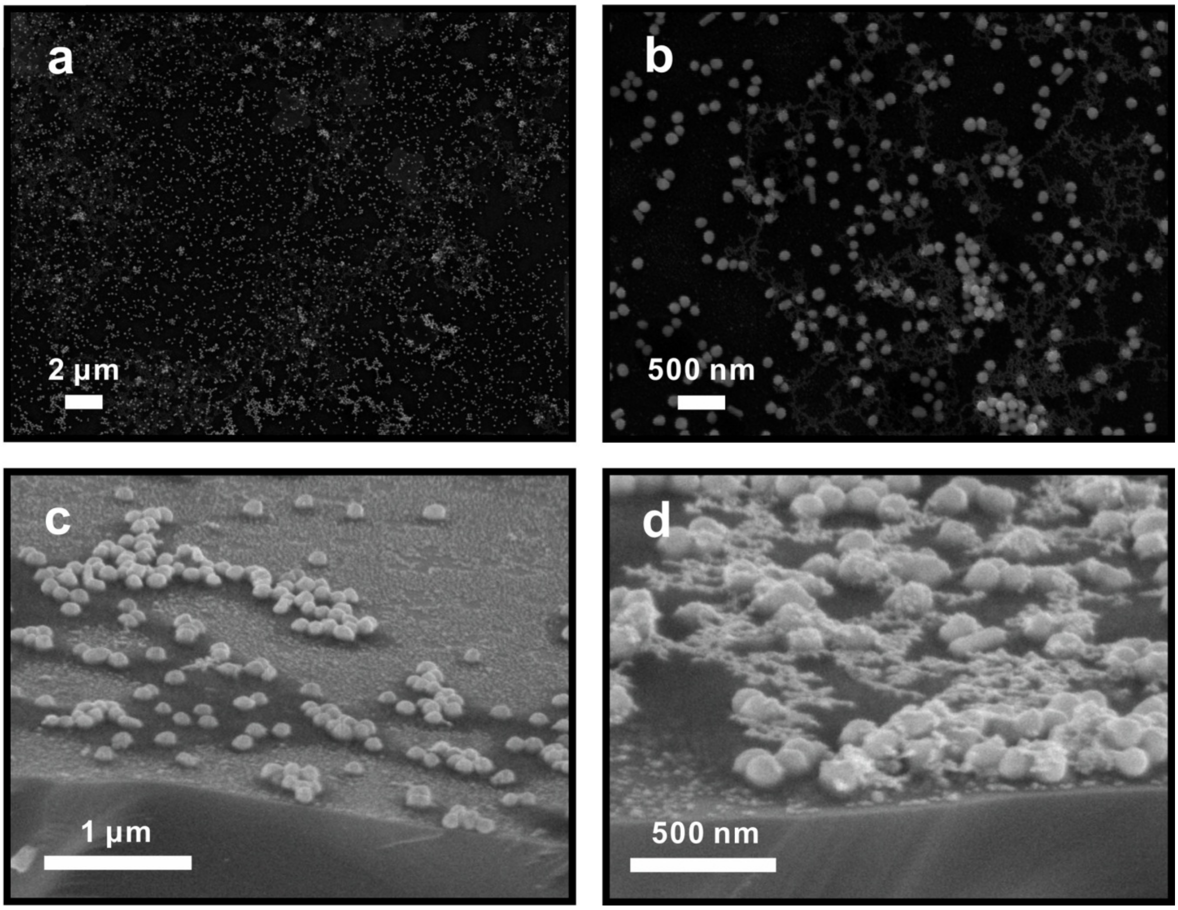


Figure S6. (a, b) Top view and (c, d) side view SEM images of solution of 10-nm and 100-nm Au NP mixture drop-casted on Si wafer and dried in air.

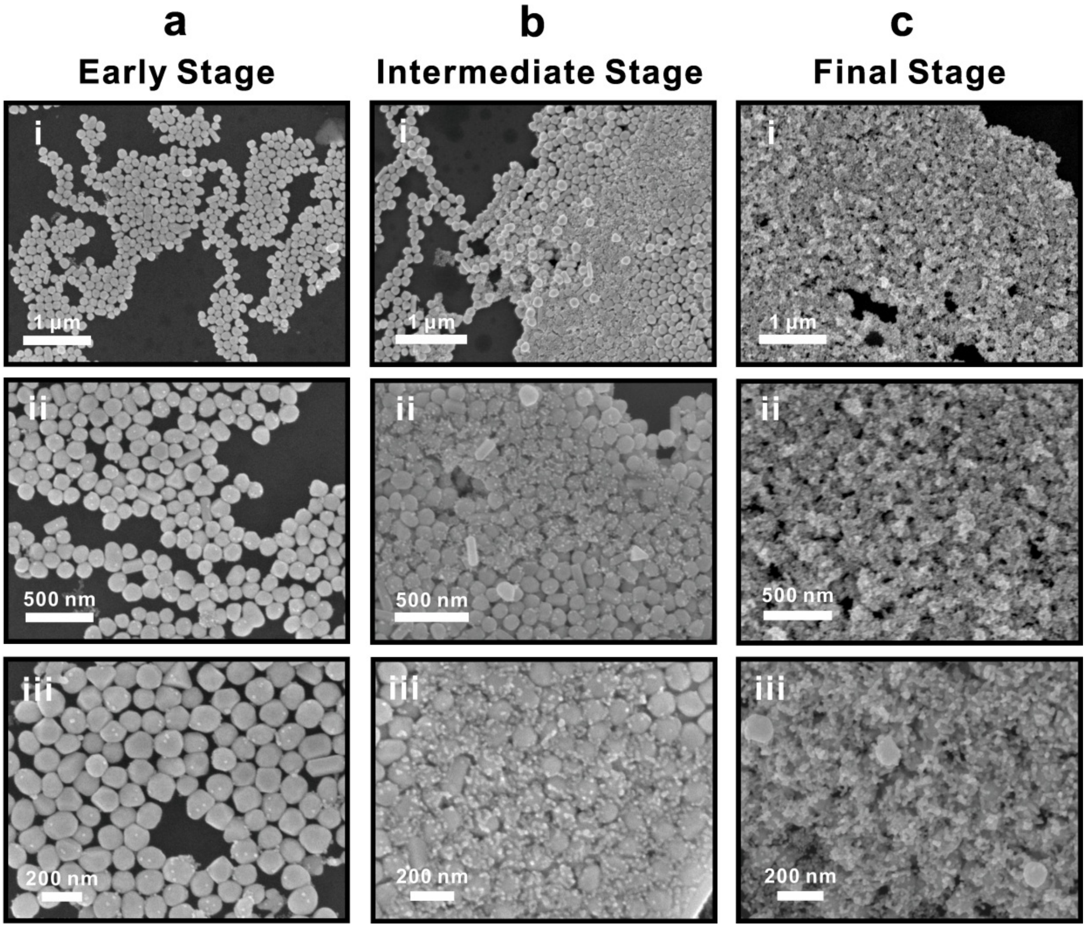
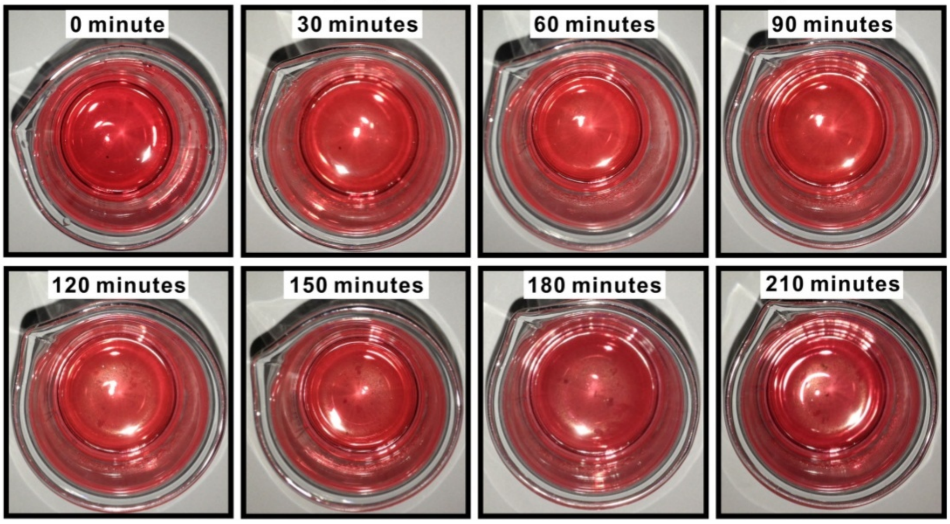
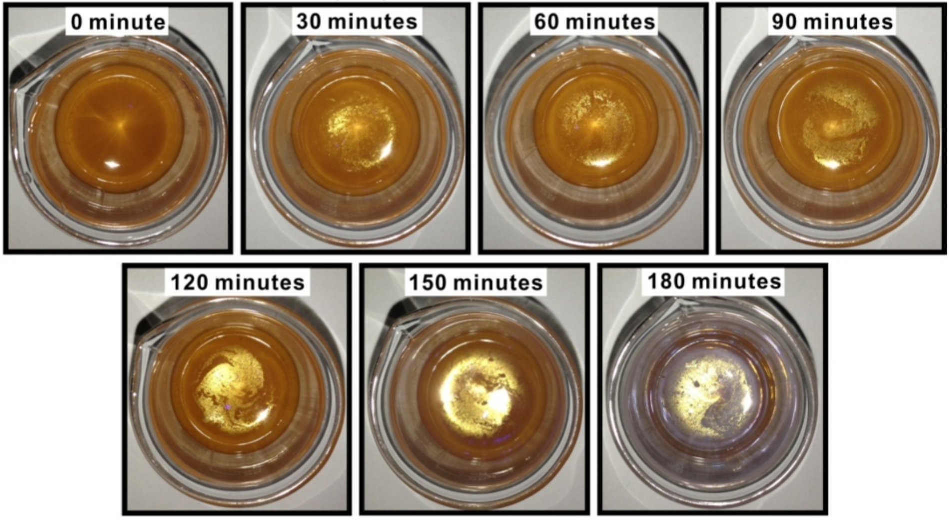


Figure S7. Additional SEM images of 10-nm/100-nm Au NP film formation at early, intermediate and final stage.


10-nm Au NPs(aq) exposed to formic acid vapor


100-nm Au NPs(aq) exposed to formic acid vapor

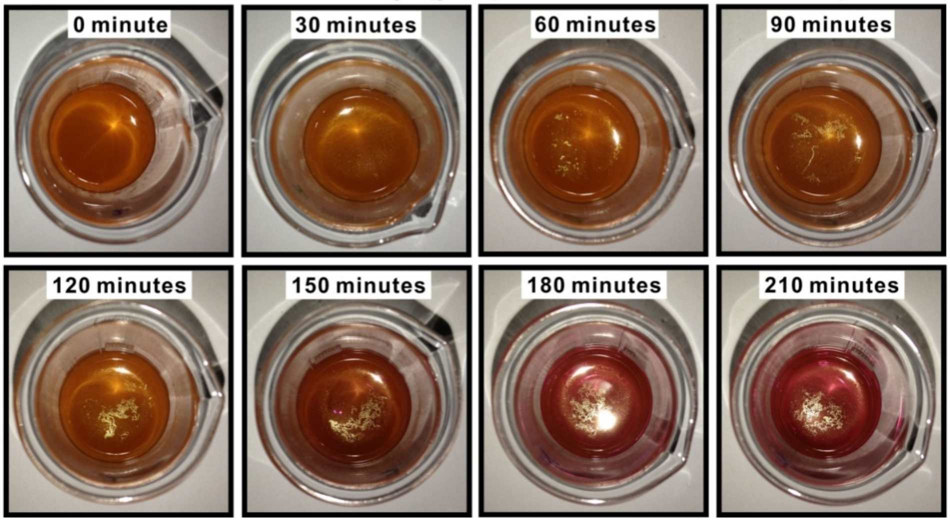

10-nm/100-nm Au NPs(aq) exposed to formic acid vapor

Figure S8.10-nm Au NPs (aq), 100-nm Au NPs (aq) and mixture of 10-nm/100-nm Au NPs (aq) solutions were separately incubated in three desiccators filled with formic acid vapor. Optical pictures were taken at different time points.

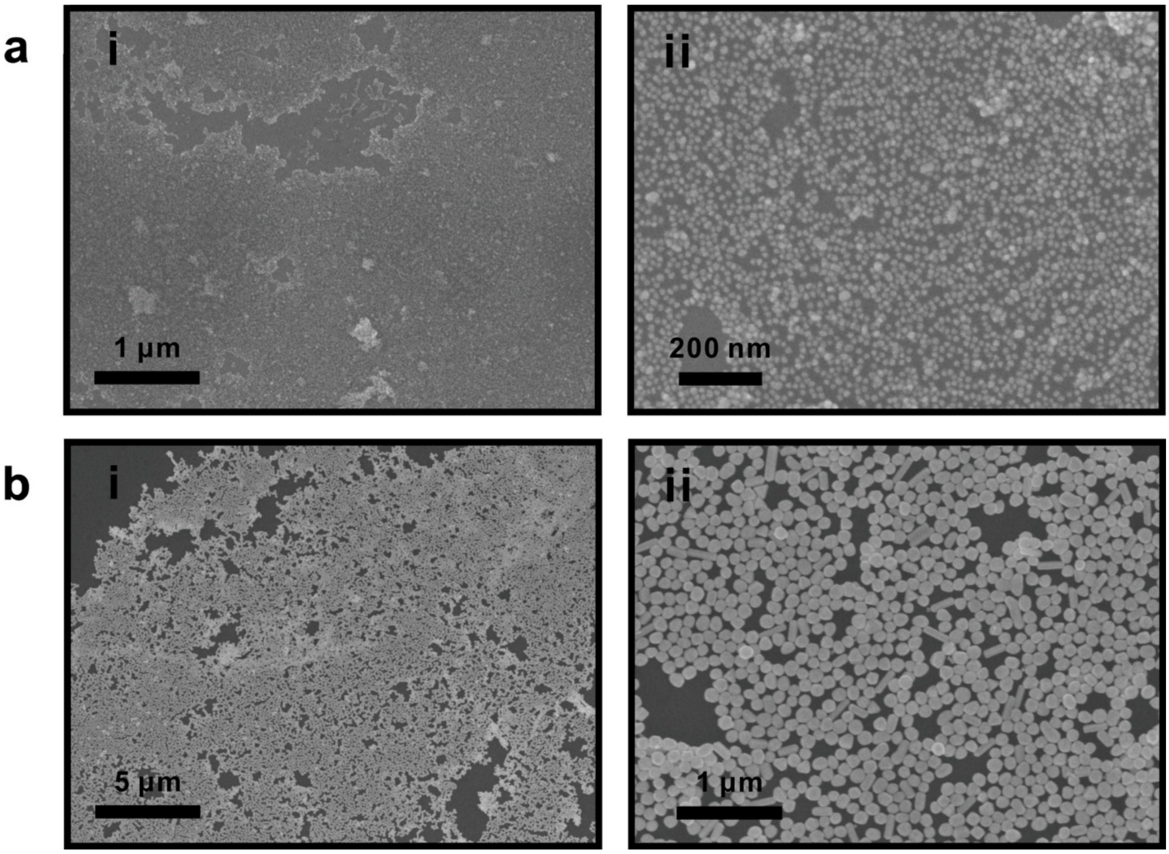


Figure S9. (a) SEM images of 10-nm Au NP film formed at water/air interface after incubating with formic acid vapor for 3.5 hours. (b) SEM images of 100-nm Au NP film formed at water/air interface after incubating with formic acid vapor for 3 hours.

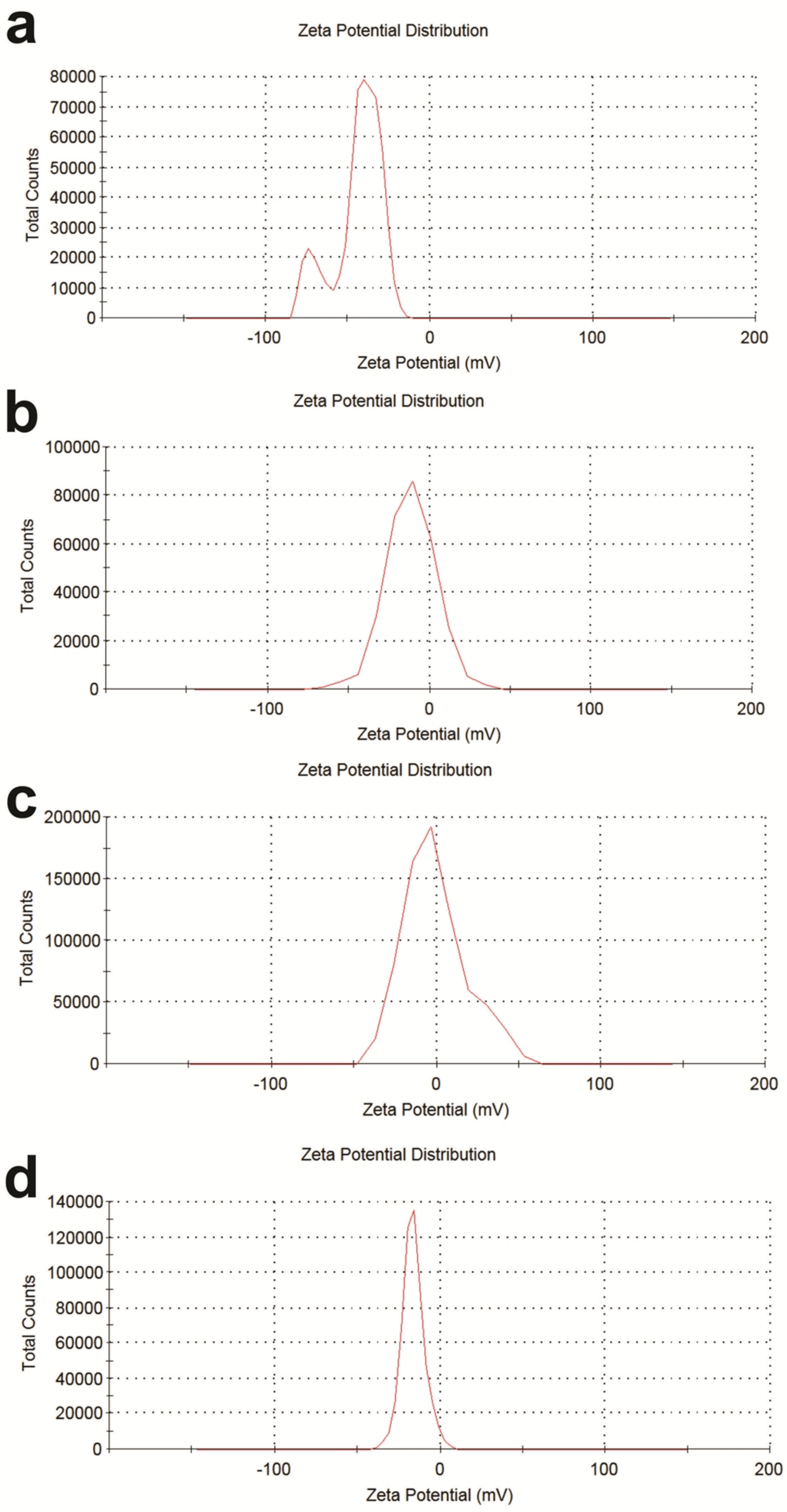


Figure S10. Zeta potential (ζ) of as-prepared 10-nm and 100-nm Au NPs. (a) Zeta potential (ζ) of as-prepared 10-nm Au NPs (aq) is -45.6 mV. Zeta potential of 10-nm AuNPs (aq) incubating in the formic acid vapour after (b) 2 hours (ζ= -11.4 mV); (c) 6 hours (ζ= -0.82 mV). (d) Zeta potential (ζ) of 100-nm Au NPs (aq) is-20.6 mV.

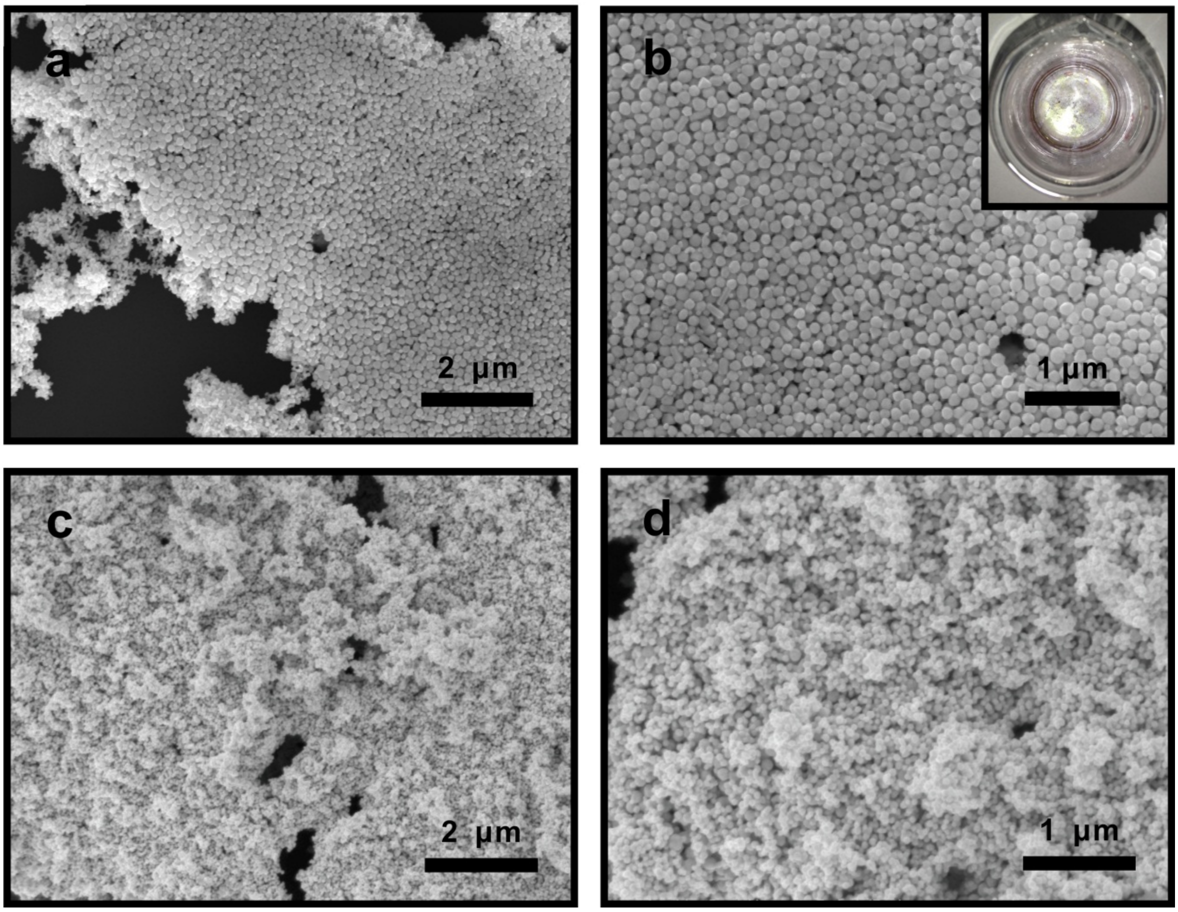


Figure S11. (a-b) Top view SEM images of 50-nm/100-nm Au NP layered structures after incubating with formic acid vapor for one day. (c-d) Back view SEM images of 50-nm/100-nm Au NP layered structures. The inset image in (b) is optical image of 50-nm/100-nm Au NP thin film.

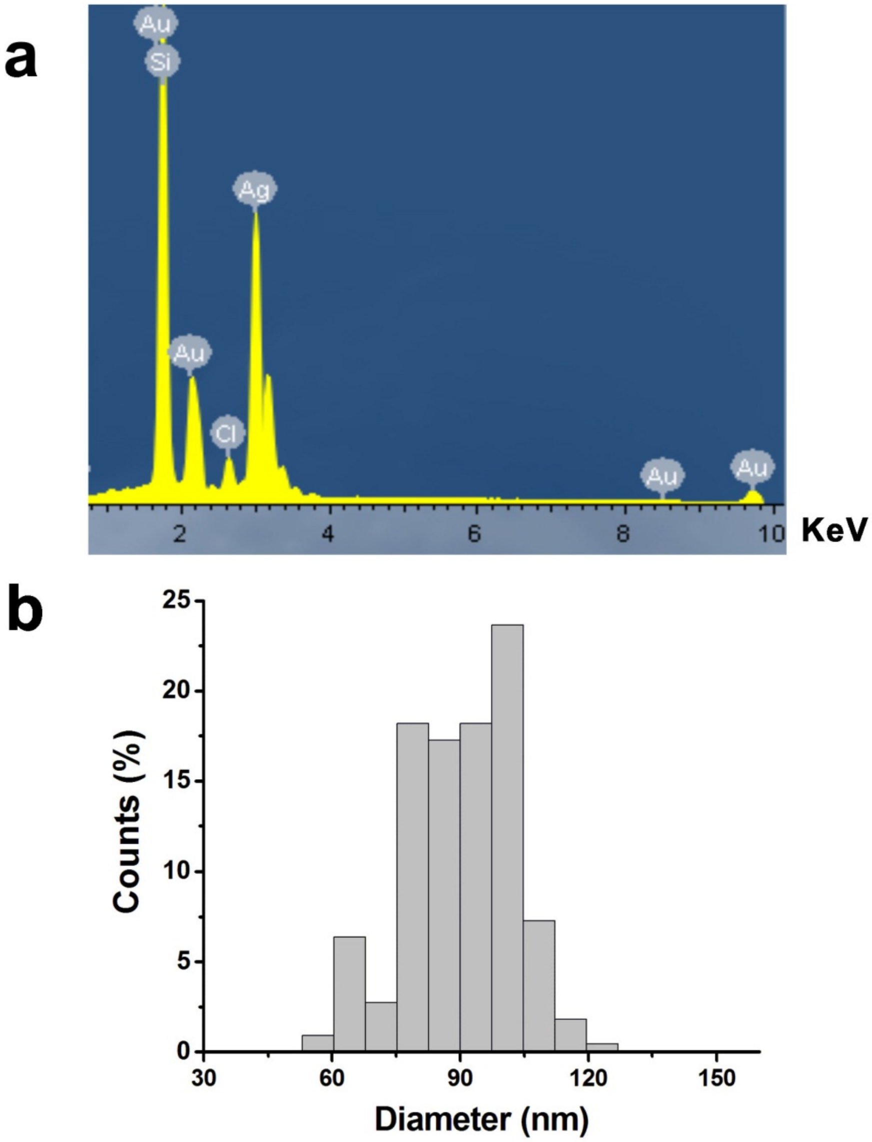
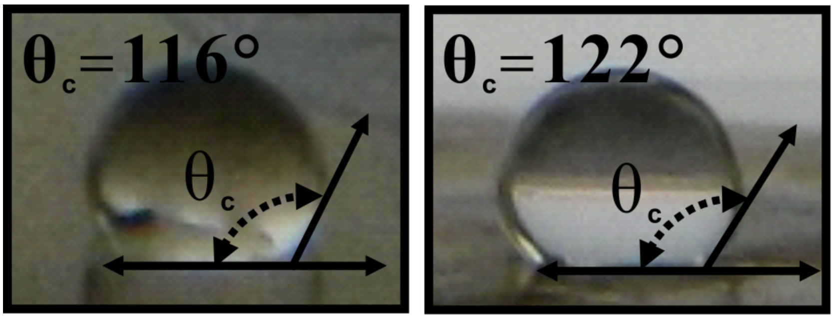
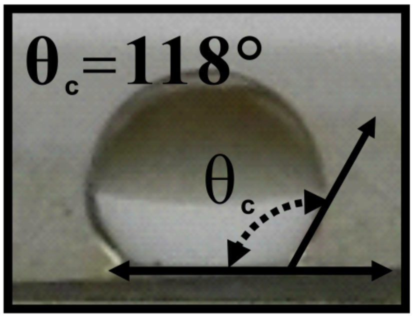


Figure S12. (a) EDS data for 30-nm Au NP/90-nm Ag NP double-layer film (Si is from the substrate). (b) Diameter distribution of as-synthesized Ag NPs (based on 110 counts; diameter = 91.3 ± 13.7 nm).



Assembled 10-nm AuNP film

Assembled 50-nm AuNP film



Assembled 100-nm AuNP film

Figure S13. Contact angles measured on self-assembled 10-nm, 50-nm and 100-nm Au NP film.

6. Reference

1. D. Qin, Y. Xia and G. M. Whitesides, *Nat. Protocols*, 2010, **5**, 491-502.
2. K. R. Brown, D. G. Walter and M. J. Natan, *Chemistry of Materials*, 1999, **12**, 306-313.
3. J. A. Dieringer, R. B. Lettan, K. A. Scheidt and R. P. Van Duyne, *Journal of the American Chemical Society*, 2007, **129**, 16249-16256.
4. R. N. Wenzel, *Industrial & Engineering Chemistry*, 1936, **28**, 988-994.
5. S. K. Ghosh and T. Pal, *Chemical Reviews*, 2007, **107**, 4797-4862.
6. P. K. Jain, K. S. Lee, I. H. El-Sayed and M. A. El-Sayed, *The Journal of Physical Chemistry B*, 2006, **110**, 7238-7248.