Nanoscale force induced size-selective separation and self-assembly of metal nanoparticles: sharp colloidal stability thresholds and hcp ordering

Yuanhui Zheng,[a] Cecilia H Lalander [b] and Udo Bach*[a,b]

[†]*Department of Material Engineering, Monash University, Wellington Rd, Clayton, VIC 3800, Australia*
[‡]*Department of Chemistry, Monash University, Wellington Rd, Clayton, VIC 3800, Australia*

ESI-1. Experimental Details

Chemicals. Unless otherwise stated, all chemicals were purchased from Sigma-Aldrich and used with further purification.

Separation of binary AuNP mixtures. In a typical procedure, 114 μL of 20 nm citrate capped gold nanoparticles (AuNPs: Ted Pella) and 886 μL of 40 nm citrate capped AuNPs (Ted Pella) were mixed (particle ratio ≈ 1:1) and concentrated to 100 μL by centrifugation (4000 rpm, 40 min). Subsequently, 25 μL of 1.67 mM thiol-PEG-carboxyl ($SH\text{-}C_{11}H_{22}\text{-}(OCH_2CH_2)_6\text{-}OCH_2COOH$: Prochimia) aqueous solution was added into the above binary AuNP mixtures. Left to react overnight followed by addition of 5 μL of 2.5% Tween 20, 65 μL of ethanol and 130 μL of 1.5 M NaCl solution. The solution was held at room temperature for 12 hours to allow for the precipitation of larger AuNPs. The supernatant containing the 20 nm AuNPs was decanted from the precipitate (40 nm AuNPs). Supernatant and precipitate were washed three times by centrifugation and redispersion in ultrapure water (18.2 MΩ·cm).

Self-assembly of thiol-PEG-carboxyl functionalized AuNPs. In a typical procedure, a Si substrate was cleaned with Piranha solution (3:1; H_2SO_4: H_2O_2) (***Note:*** Piranha solution is highly corrosive and should be handled with extreme caution.) and then immersed in a mixture of 4 μL of 3-aminopropyltriethoxysilane (APTES, Sigma-Aldrich Chemical Co.), 190 μL of ethanol, and 6 μL of ultra pure water for 1 hour. The substrate was washed with ethanol three times and then baked at 110 °C for 10 min. For self-assembly experiments, 2 μL of NaCl solution (0.2 M for sediment and 5.0 M for supernatant) and 2 μL of the gold colloids, obtained after the separation, were added on the APTES modified Si substrate. The substrate was put in a humidity chamber (Corning Incorporated, Corning) for 3 hours and then washed with water three times.

ESI-2. Stability of SH-PEG-COOH modified AuNPs

(a) Temperature effect. Citrate capped AuNPs (40 nm) were concentrated from 2 mL to 200 µL by centrifugation (4000 rpm, 40 min). Subsequently, 50 µL of 1.67 mM thiol-PEG-carboxyl solution was added and the solution was kept at room temperature overnight. Small volumes (20 µL) of the PEG-carboxyl functionalized AuNP was transferred into a 1.7 mL centrifuge tube and 10 µL of ethanol and 20 µL of NaCl solution of a given concentration were added and left to react for 3 h at 4 ºC and room temperature, respectively. Following precipitation the supernatant was decanted and 200 µL of ultra pure water added to redisperse the AuNPs.

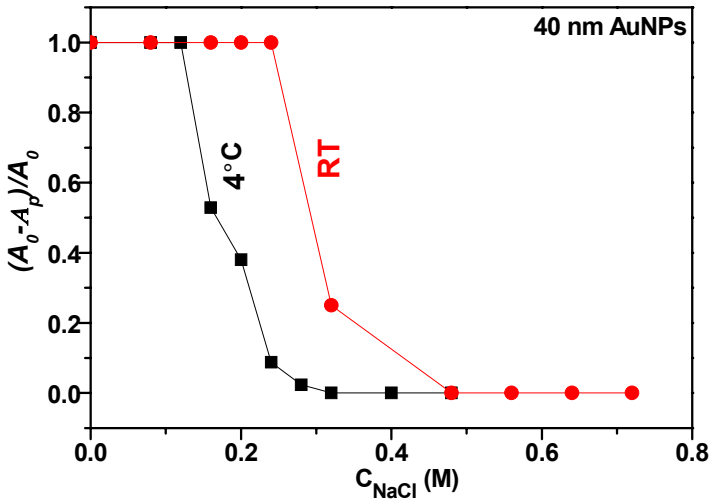

Figure S1. *Salt concentration dependent colloidal stability of thiol-PEG-carboxyl capped AuNP solutions with particle size of 40 nm at room temperature (red circle) and 4 ºC (black squares). The stability (S) of the colloidal AuNP solutions is determined by the following equation: $S=(A_0-A_p)/A_0$, where A_0 and A_p are the absorbances at 530 nm of the 'initial' AuNP solution in ultrapure water and the precipitated particles redispersed in water with the same volume of the 'initial' AuNP solution.*

(b) Thiol-PEG-carboxyl concentration effect. Citrate capped AuNPs (40 nm) were concentrated from 2 mL to 200 µL (4000 rpm, 40 min) and 50 µL of *x* mM (*x* = 0.33 and 1.67) thiol-PEG-carboxyl solution added. The solutions were kept at room temperature overnight, whereupon 20 µL of the PEG-carboxyl functionalized AuNP was transferred into a 1.7 ml centrifuge tube. Subsequently 10 µL of ethanol and 20 µL of NaCl solution of a given concentration were added and the mixture left to react at room temperature for 3 hours. Following precipitation the supernatant was decanted and 200 µL of ultra pure water added to redisperse the AuNPs.

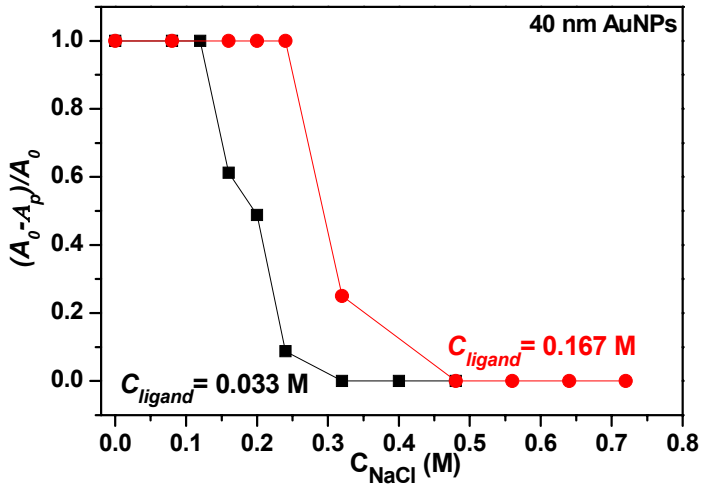

Figure S2. *Salt concentration dependent colloidal stability of 40nm AuNPs synthesized at different concentrations of thiol-PEG-carboxyl (red circle: 0.167 M and black squares: 0.033 M). The stability (S) of the colloidal AuNP solutions is determined by the following equation: $S=(A_0-A_p)/A_0$, where A_0 and A_p are the absorbances at 530 nm of the 'initial' AuNP solution in ultrapure water and the precipitated particles redispersed in water with the same volume of the 'initial' AuNP solution.*

(c) Solvent composition effect. Citrate capped AuNPs (20 nm) were concentrated from 2 mL to 200 µL (4000 rpm, 40 min) followed by addition of 50 µL of 1.67 mM thiol-PEG-carboxyl. The mixture was kept at room temperature overnight, whereupon 20 µL of PEG-carboxyl functionalized AuNP was transferred into a centrifuge tube. Subsequently *x* µL (*x* =10, 20, 25, and 30) of ethanol and 20 µL of NaCl solution of a given concentration were added. The mixture was held at room temperature for 3 hours upon which the supernatant was decanted from the precipitate and 200 µL of ultra pure water added to redisperse the AuNPs.

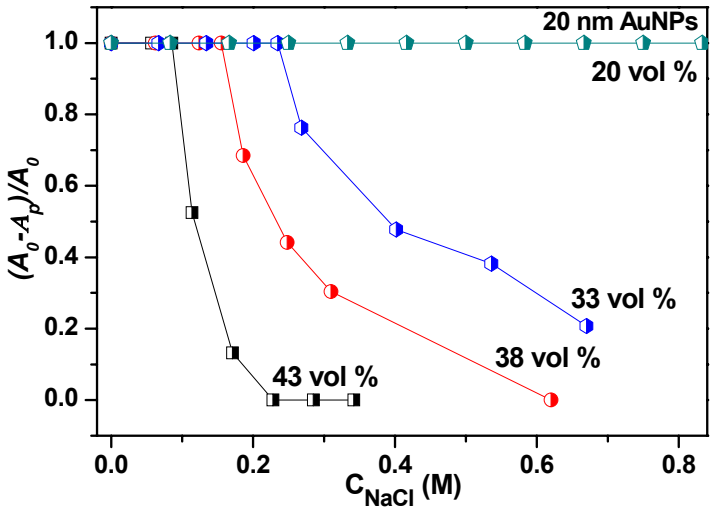

Figure S3. *Salt concentration dependent colloidal stability of thiol-PEG-carboxyl capped AuNP solutions with particle size of 20 nm at different ethanol contents. The stability (S) of the colloidal AuNP solutions is determined by the following equation: $S=(A_0-A_p)/A_0$, where A_0 and A_p are the*

absorbances at 530 nm of the 'initial' AuNP solution in ultrapure water and the precipitated particles redispersed in water with the same volume of the 'initial' AuNP solution.

ESI-3. SEM-image based statistical analysis of particle size distribution

1) Mixed AuNP colloids

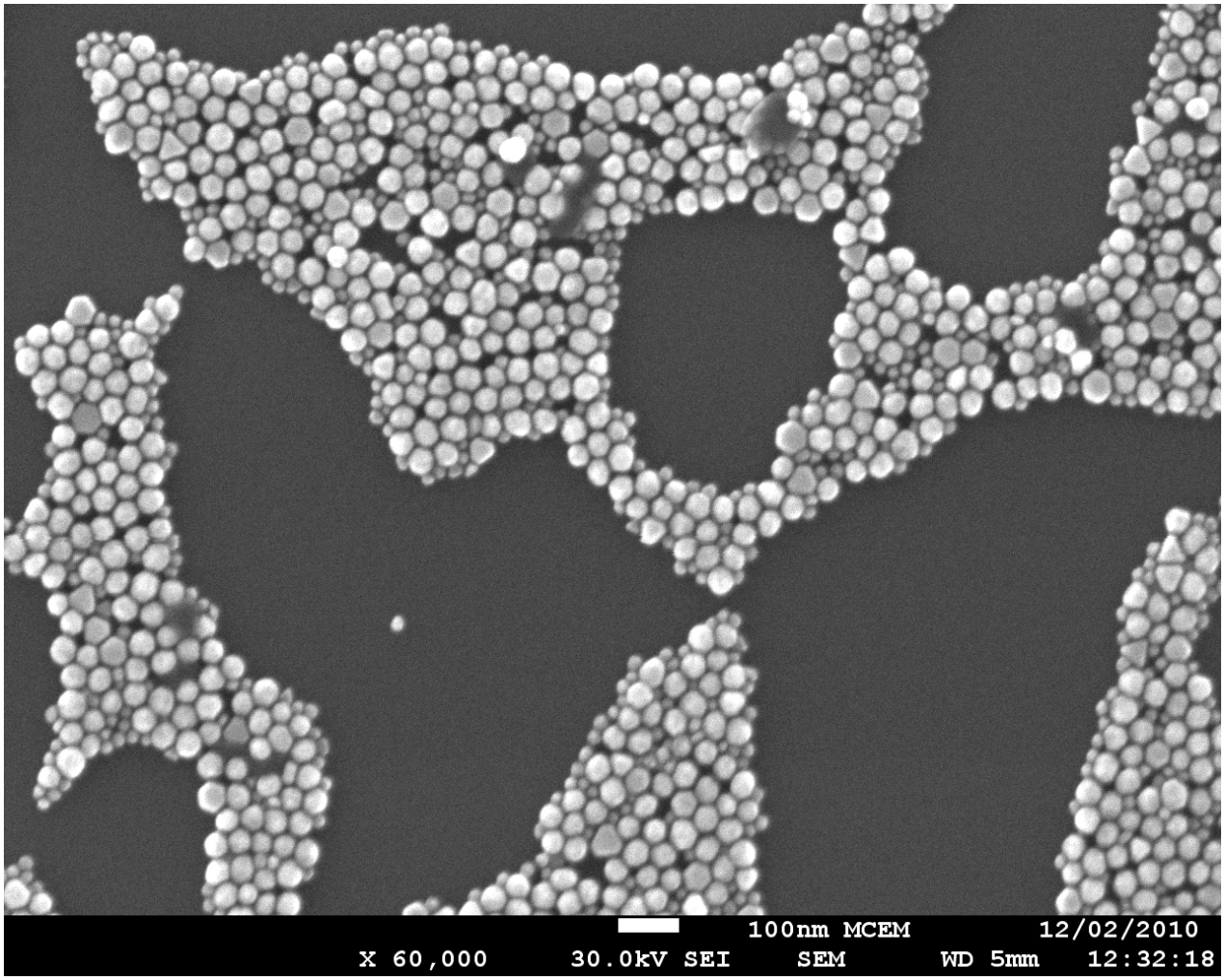

Figure S4. *SEM image of AuNPs with bimodal particle size distribution (20 and 40 nm diameter) prior to the separation. The AuNPs were self-assembled onto an APTES-modified Si(100) wafer through electrostatic interaction. There are 489 small particles and 660 large particles in the SEM image.*

2) Redispersed precipitate

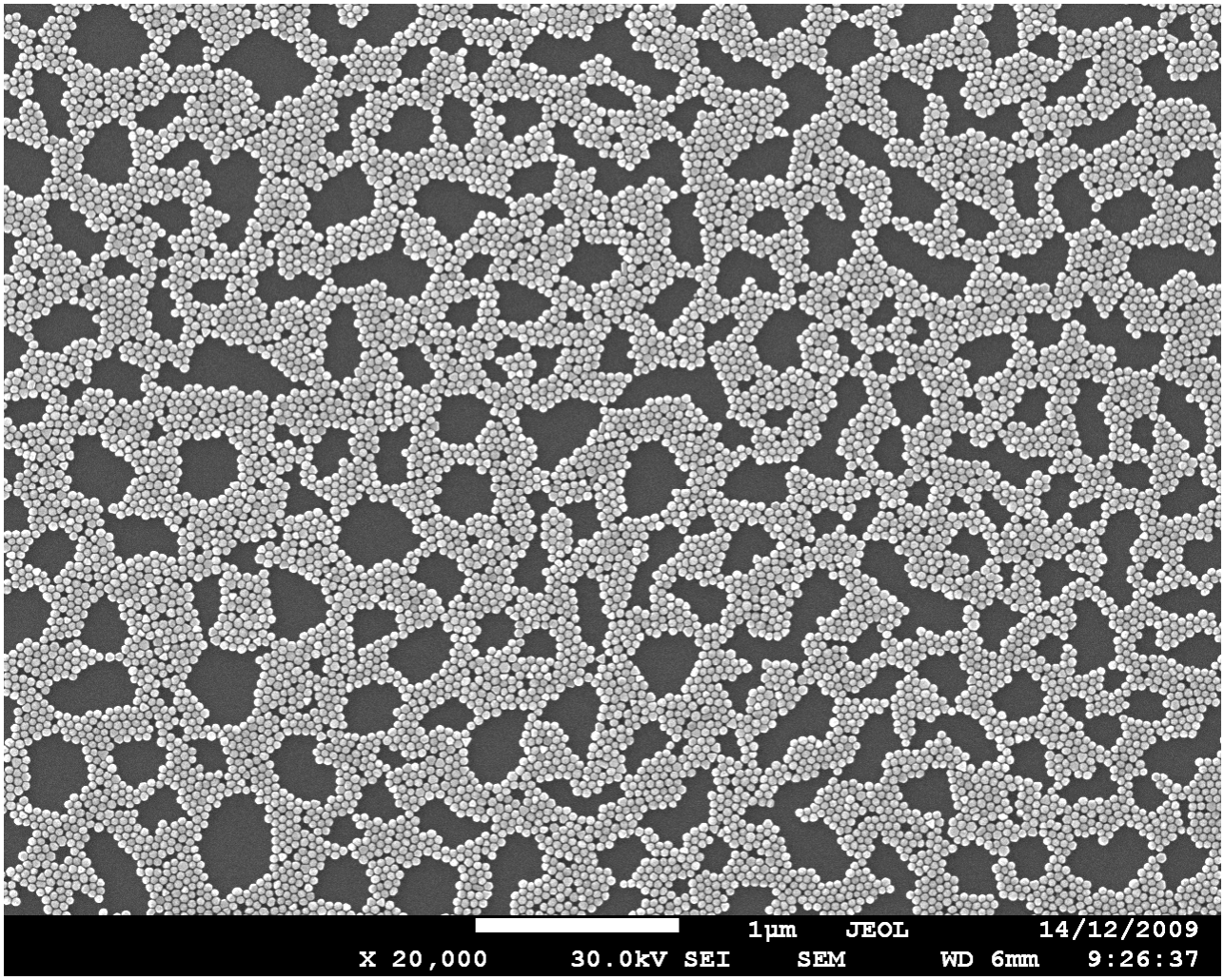

Figure S5. *SEM image of AuNPs from the redispersed precipitate. The AuNPs were self-assembled onto an APTES-modified Si(100) wafer through electrostatic interaction. There are 26 small particles and 10,162 large particles in the SEM image.*

3) Supernatant

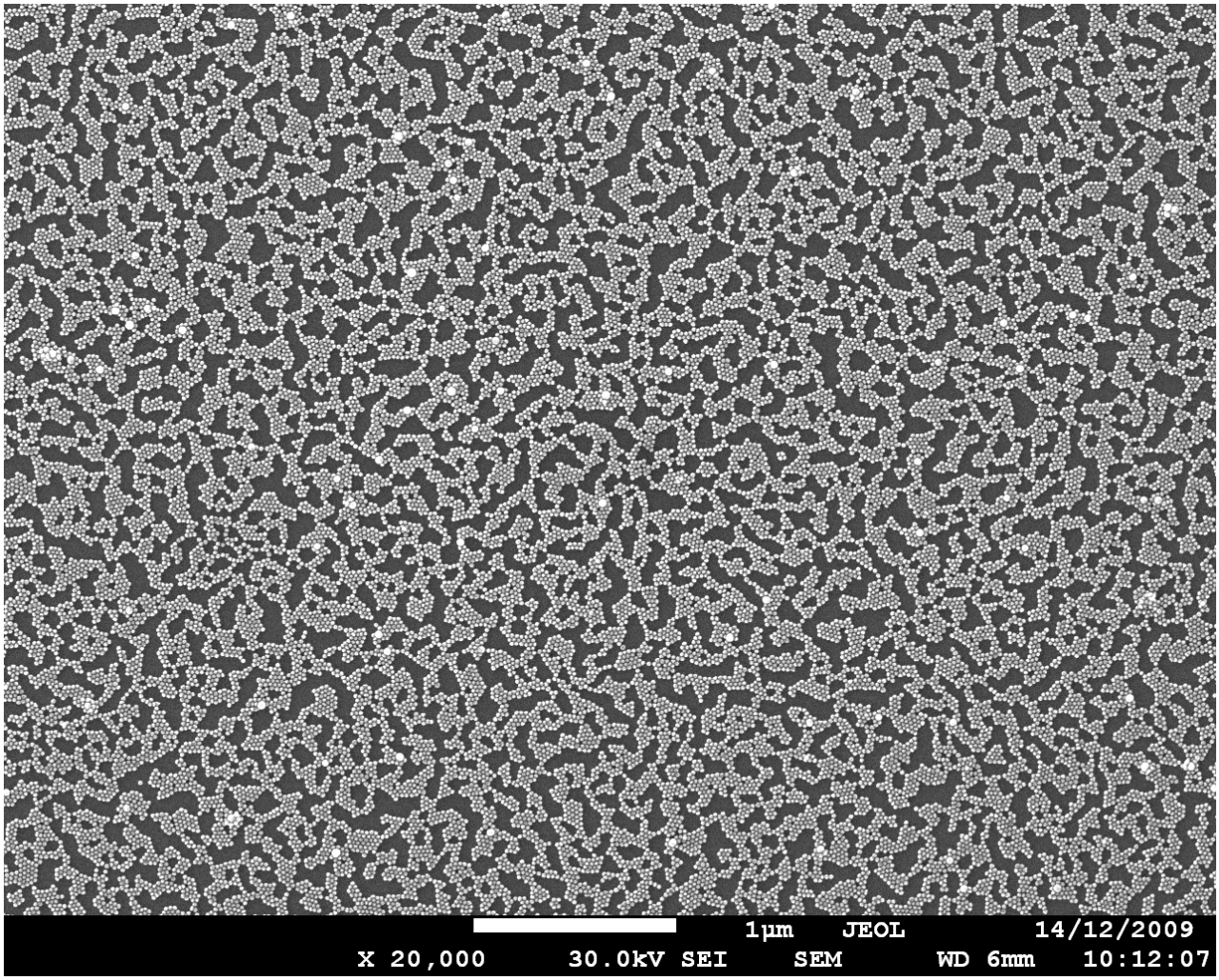

Figure S6. *SEM image of AuNPs from the supernatant. The AuNPs were self-assembled onto an APTES-modified Si(100) wafer through electrostatic interaction. There are 13,734 small particles and 83 large particles in the SEM image.*

ESI-4. SEM images of precipitated AuNPs

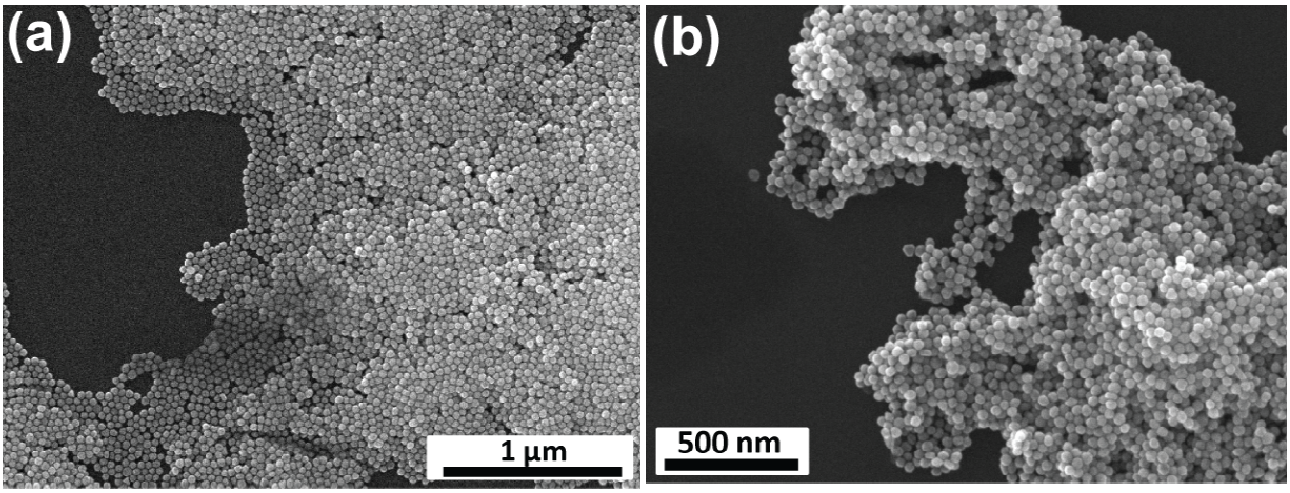

Figure S7. *SEM images of the precipitated AuNPs: (a) thiol-PEG-carboxyl modified AuNPs and (b) citrate-capped AuNPs.*

It is worth noting that the thiol-PEG-carboxyl modified AuNP precipitates on the Si(100) wafer show metallic color while citrate-capped AuNP agglomerates show black color. The SEM image of thiol-PEG-carboxyl modified AuNP precipitates (Figure 7Sa) shows short-range 3D hcp ordering for thiol-PEG-carboxyl modified AuNP precipitates, indicating that "colloidal crystallization" happened during the precipitation process. The 3D hcp ordering was not observed for citrate-capped AuNPs precipitated under the same conditions (Figure S7b).