Supplemental

Mechanistic Investigation of Seeded Growth in Triblock Copolymer Stabilized Gold Nanoparticles

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Synthesis of Citrated Gold Nanoparticles

The detailed synthesis protocol is described elsewhere.[1] Briefly, 150 mL of 2.2 mM trisodium citrate solution was refluxed for 15 min followed by the rapid addition of $HAuCl_4$ (1mL; 25 mM) until the solution turned soft pink (~10 min). The solution was cooled to 90 ºC and trisodium citrate (4 mL; 15 mM) and $HAuCl_4$ (1 mL; 25 mM) were injected sequentially followed by additional refluxing (~30 minutes). This injection of trisodium citrate (4 mL; 15 mM) and $HAuCl_4$ (1 mL; 25 mM)) was repeated until 14 generations of progressively larger gold nanoparticles were synthesized. After each stage, 5 mL aliquots were removed for further characterization.

Purification by Diafiltration. We used an additional purification step of diafiltration for seed citrated GNPs. Diafiltration is an efficient and convenient method for purification and size selection of water-soluble nanoparticles, and to remove the excess citrate in the solution after reduction.[2] An equal volume of water used to replace the initial volume. The dialysis pump was obtained from SciLog (PureTec CP-120). Poly-(sulfone) diafiltration membranes (300 kDa; MiniMate) were obtained from Pall.

Citrated GNP Size Characterization by AFM and UV-vis/DLS. The size and concentration of the citrated and TBP coated GNPs were determined by the combination of AFM height and UV/vis measurements. We found excellent correspondence between the measured AFM Z-height (22.5 ± 1.4 nm) and the value (23 nm) determined from the 450 nm absorbance using empirical equations derived by Haiss and coworkers.[3] This enabled us to estimate the GNP concentration. DLS confirmed also that the citrated GNP seeds were monodisperse (< 10%; Figure S1).

Sample Preparation for AFM and STEM

To obtain effective particle dispersion and attachment of negatively charged GNPs on both mica (15 mm radius) disks and coated Cu grids (Ted Pella 200 mesh) pretreatment with freshly made APTS (0.1% v/v) solution was necessary to produce a positively charged surface. A stock solution 10 μL APTS in 10 mL DI water can be prepared and stored at 4 °C. In preparation for AFM measurements, a freshly cleaved mica sheet is covered with APTS (0.1% v/v; 500 μL) solution. Similarly, a Cu grid is placed on APTS (0.1% v/v; 50 μL) droplet created on a hydrophobic surface (parafilm M^{TM}). After approximately one hour the surfaces are gently washed with ethanol then water. GNP samples were prepared for AFM and FESEM/STEM measurements by dilution in equal volumes of water followed by centrifugation (17,900 *g*; 5 min) then suspended in equal volumes of water. The GNPs (20 μL) are added to the modified mica surface and left to incubate for at least 30 minutes, followed by a sequential wash with ethanol and water.

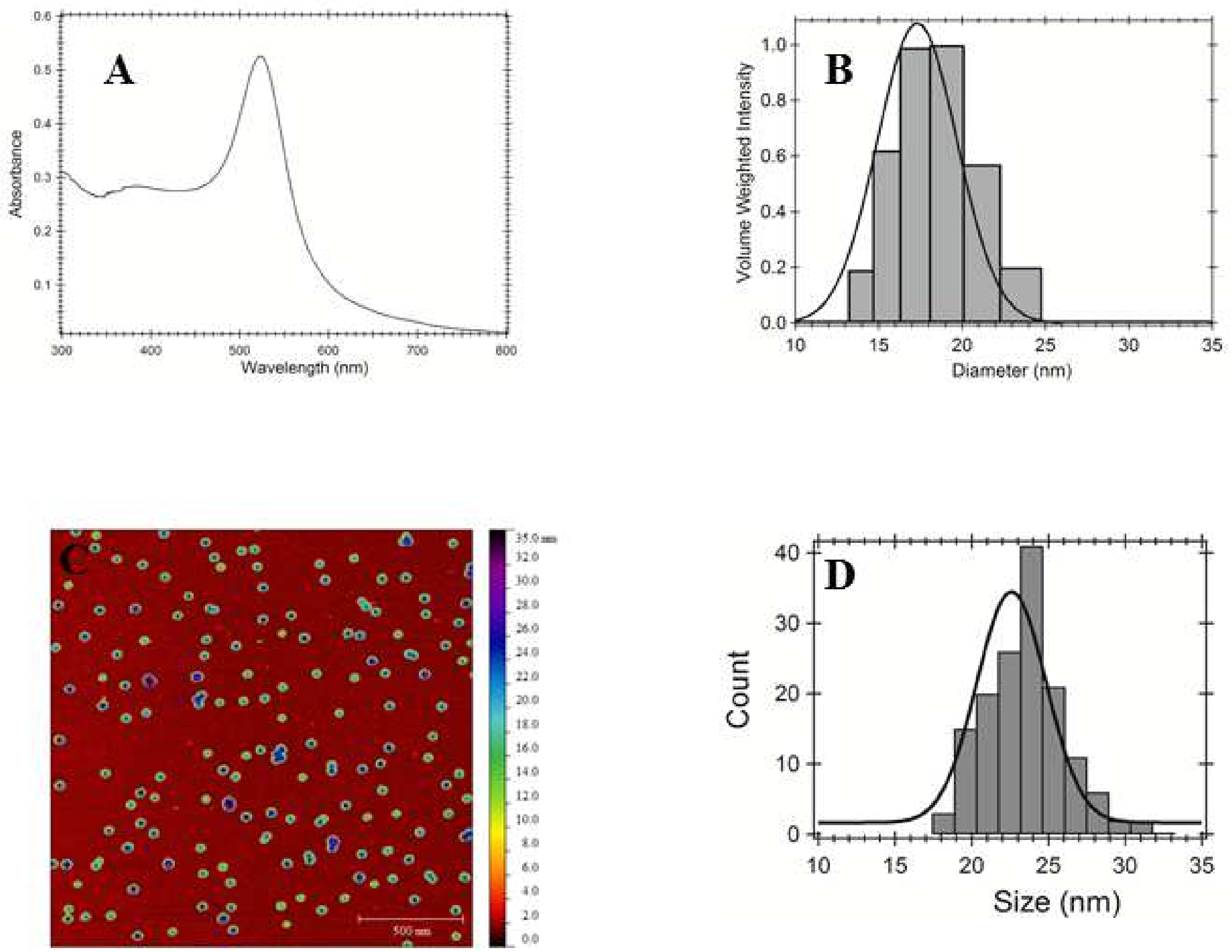

Figure S1. (A) UV-vis absorbance spectrum of the citrated GNP seeds in which the localized surface plasmon resonance (LSPR) maximum is 521 nm and $A_{spr}/A_{450} \approx 1.78$. (B) Dynamic light scattering volume weighted distribution (17.3 ±1.5) nm. (C) AFM (2 x 2 μm^2) height image. (D) AFM height distribution (22.5 ± 1.4) nm.

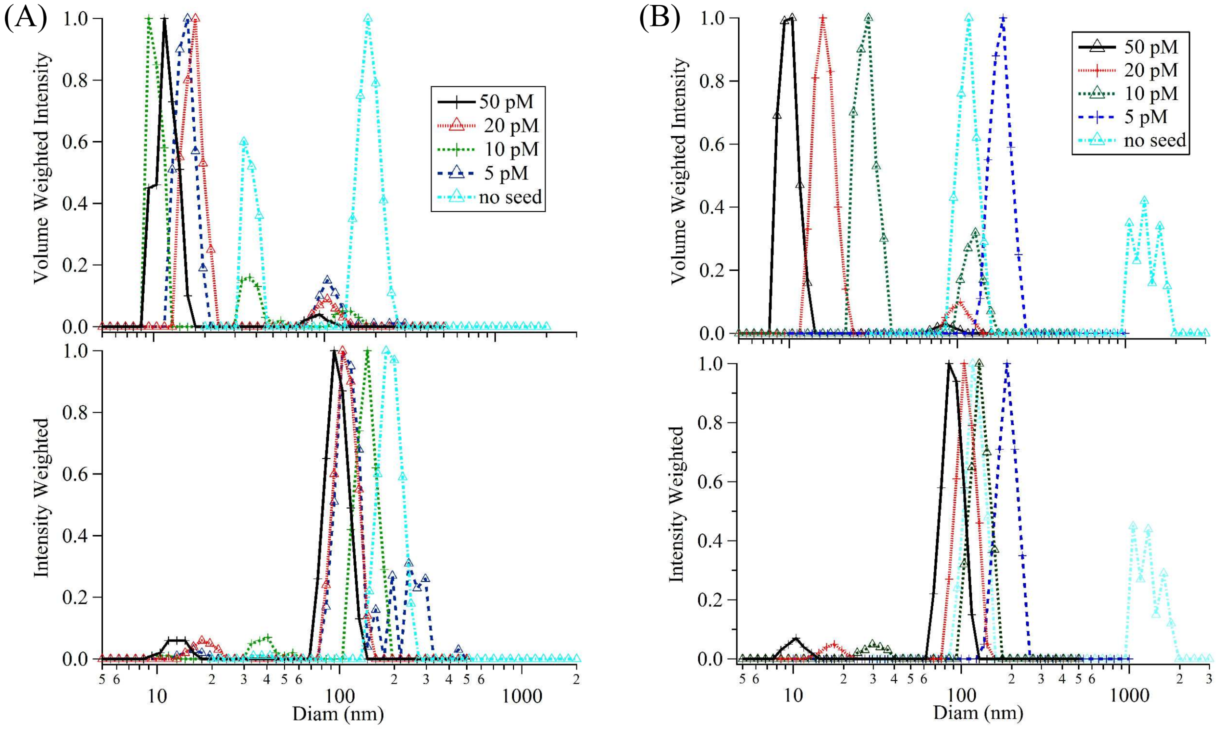

Figure S2. The mean hydrodynamic diameter distributions of the GNPs against GNP seed concentrations in aqueous solutions for (A) (4 mM)F68/(≈1 mM) Au(III) and (B) (4 mM)F68/(8 mM)L31/(≈1 mM) Au(III).

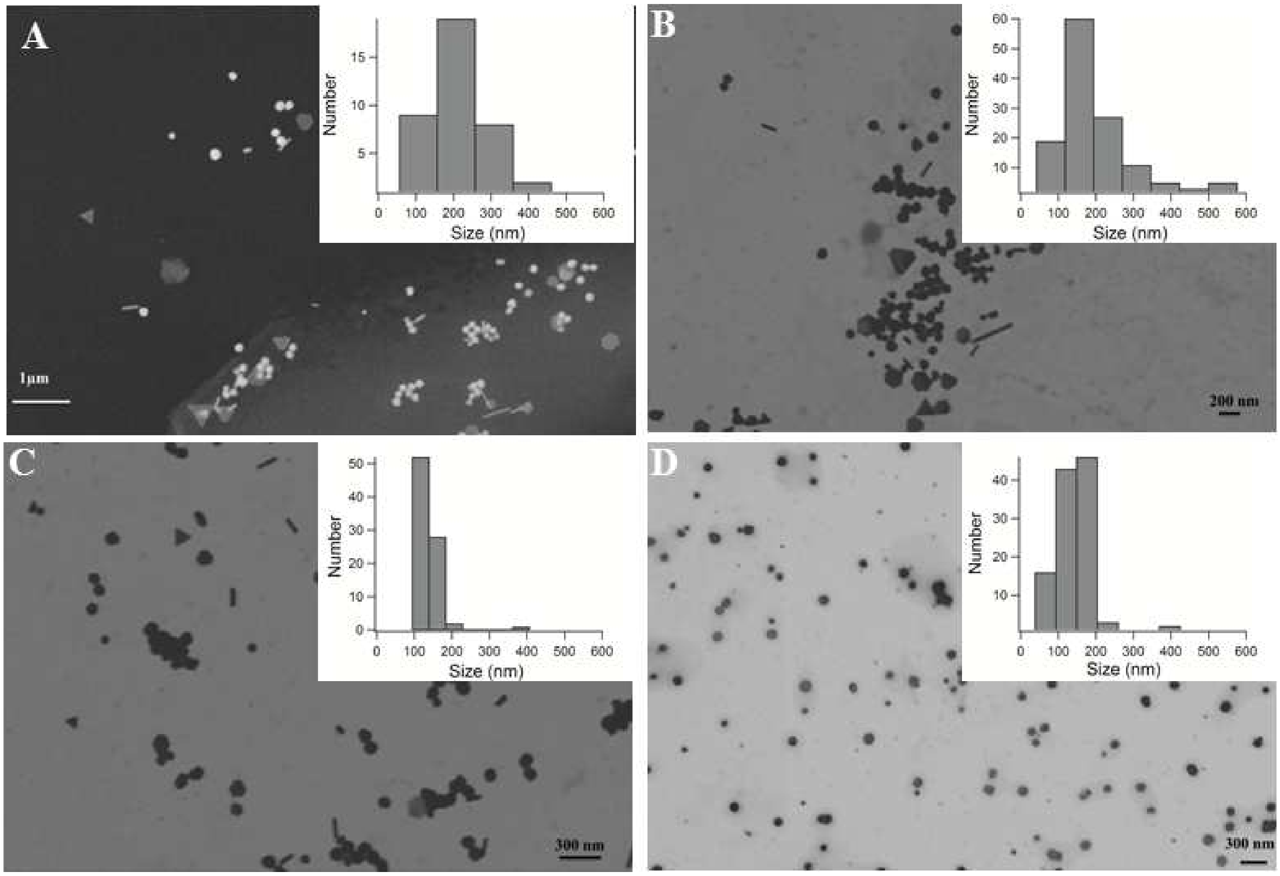

Figure S3. Electron micrographs and histograms of the bigger size population TBP coated GNPs at (A) 5 pM (168 ± 123 nm), (B) 10 pM (165 ± 120 nm), (C) 20 pM (117 ± 34 nm), and (D) 50 pM (110 ± 41 nm) GNP seed concentrations.

Chemical Modification of TBP coated GNPs

Thiolated GNPs were produced by ligand substitution of the TBP coated GNPs. We tried two approaches to functionalize the GNPs. Equal volumes of GNP solution (unwashed) and 10 mM of phosphate buffer were mixed. MUA (1 mM in ethanol) was added to this mixture for a final 1:10 volume ratio. For example, 1 mL of MUA solution is added to 10 mL solution containing 5 mL of GNP solution and 5 ml phosphate buffer (10 mM) solution. The solution was left for 24 to 48 hours in the dark. Then the solution was washed by centrifugation several times.

Diafiltration. GNP purification by centrifugation is not an efficient method for removal of the excess polymer and thiol. A more effective approach employed diafiltration that uses a tangential filter to wash the GNPs prior to adding MUA. The dialysis pump was obtained from SciLog (PureTec CP-120) to remove the excess TBP in the solution after reduction. Poly-(sulfone) diafiltration membranes (300 kDa; MiniMate) were obtained from Pall. Sweeney et al.[2] found also that diafiltration was an efficient and convenient method for purification and size selection of water-soluble nanoparticles. In this protocol, the GNPs were diafiltered with four times the initial volume (50 mL starting solution) and suspended in 5 mM phosphate buffer or water. In a typical preparation, the amount of MUA (1 mM in ethanol) to GNP solution is 1:10 (e.g. 1 mL MUA in 10 mL GNP solution). Attenuated total reflection ATR-FTIR (JASCO 400 instrument at 4 cm^{-1} resolution with a germanium crystal) of the thiolated GNPs was done to confirm the presence of carboxylate groups on the surface (Figure S4).

The UV-vis spectra demonstrate that after 48 hours in solution, there is no further aggregation as evidenced by the negligible shift in the LSPR peak (Figure S4A). The FTIR spectra confirm the covalent attachment of thiol to the GNP due to the absence of the S-H mode expected at ~ 2500 cm^{-1} (Figure S4B).

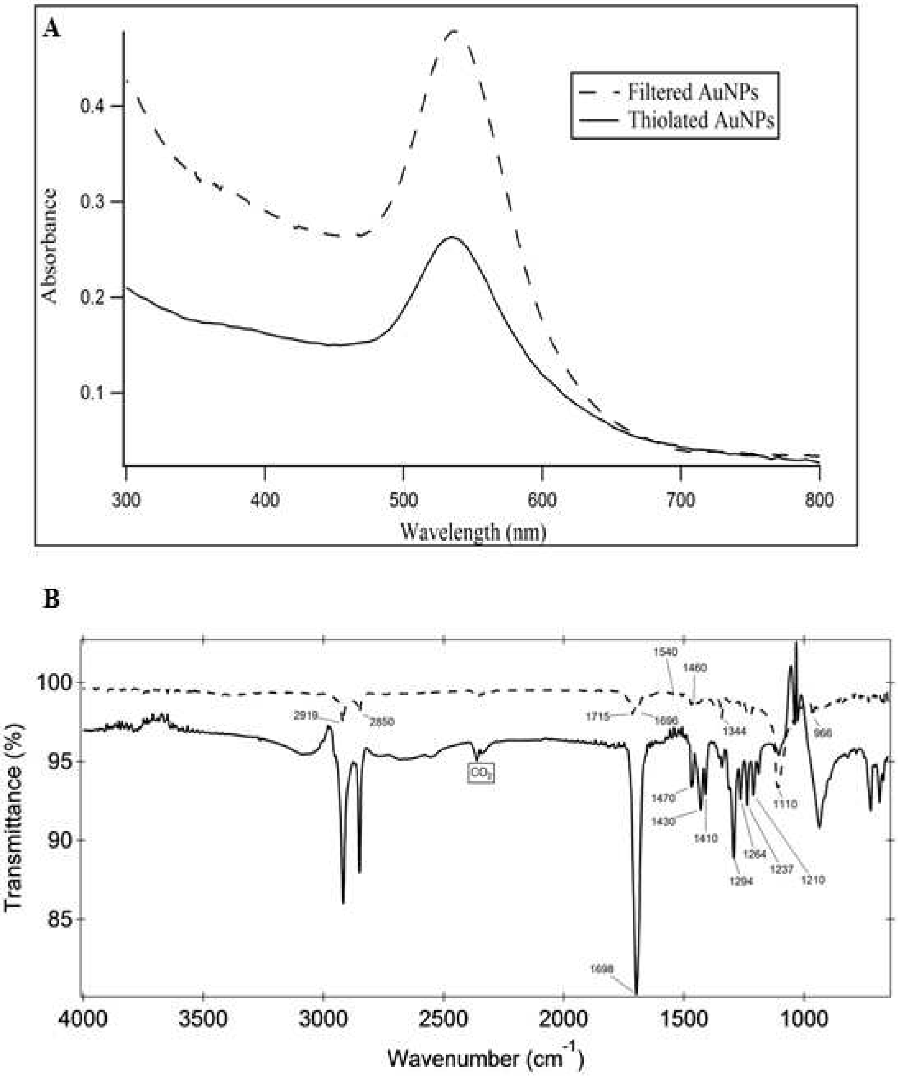

Figure S4. Characterization of the MUA functionalized AuNPs. (A) UV-vis and (B) ATR-FTIR of MUA (solid lines) and thiolated GNPs (dotted lines).

Kinetic Monte Carlo Simulation

In the Kinetic Monte Carlo approach each reaction channel is described by a propensity function, or a stochastic reaction rate. The propensity function is dependent on the current molecular populations and is a product of infinitesimal time δt. It yields the probability that the reaction will occur somewhere inside the system in the next δt.[4] Stochastic rate constants, c_s, in contrast to reaction rate constants, k, are in differential equations that contain numbers of molecules per unit volume rather than molecular concentrations. This means: 1st order $c_s = k$; 2nd order $c_s = k/V$; and 3rd order $c_s = k/V^2$.

In the simulation, we used 10^4 Au(III) atoms, which occupy a volume of $\sim 10^7$ nm^3, for an initial concentration of $\sim 10^{-3}$ M Au(III). We note that 1 nM GNP seed concentration is $\sim 10^{15}$ particles/L = 10^{12} particles/mL and is equivalent to $\approx$ 1 particle per $\sim 10^7$ nm^3. We begin by assuming a) that the reduction is a two-step process (Au(III) $\xrightarrow{0.01 s^{-1}}$ 3 Au(I) $\xrightarrow{0.01 mol^{-2} s^{-1}}$ 2 Au(0) + Au(III)), and b) that the rate of GNP growth is independent of chain length and particle size. Experimentally the first-order reduction rate constant is $\sim 10^{-2}$ s^{-1}.[5]

There are two competitive growth pathways in our seeded model: (1) GNP direct growth in solution by the coalescence of reduced gold atoms and (2) growth of gold atoms adsorbed on the surface of the seeding particles. The second order rate constants are unknown, but were set to 1 mol^{-1}s^{-1}. The maximum growth rate was obtained from the derivative of the number of gold atoms incorporated against time, while the number of particles in the cluster is determined by dividing the number of Au atoms by the number of particles (Figure S5). In this simulation, it is assumed that the collisional cross-section is size independent and that each reaction is an irreversible, stochastic process between two particle clusters. Below is a basic outline of the reaction scheme.

1. **Gold(III) Reduction:**

(S.1a) $\mathbf{Au(III)} \xrightarrow{0.01 s^{-1}} \mathbf{Au(I)}$

(S1b) $\mathbf{\mathit{3}\ Au(I)} \xrightarrow{0.01 mol^{-2} s^{-1}} \mathbf{\mathit{2}\ Au(0) + Au(III)}$

The symbols: Au(III, I, 0) are the gold in various oxidation states. The gold nanoparticle (GNP) clusters can either grow on the surface of the GNP seeds or in solution. It is assumed that the rate constants for cluster addition are size independent.

2. **Initiation:**

(solution)

(S2a) $2\ \mathrm{Au}(0) \xrightarrow{1 mol^{-1} s^{-1}} \mathrm{Au}(0)_2$

(seed surface)

(S2b) $N_s + \mathrm{Au}(0) \xrightarrow{1 mol^{-1} s^{-1}} \mathrm{Au}(0)_{ads}$

where N_s represents the available adsorption sites on the seed surface. In this simulation N_s is one per seed particle.

This step is represented in the simulation:

(S2c) $\mathbf{\mathit{2}\ Au(0)} \xrightarrow{1 mol^{-1} s^{-1}} \mathbf{Au(0)}_{\boldsymbol{n}}$ **where *n* = 2 initially**

(S2d) $\boldsymbol{N_s} + \mathbf{Au(0)} \xrightarrow{1 mol^{-1} s^{-1}} \mathbf{Au(0)}_{\boldsymbol{ads}}$

3. **Propagation:**

(solution)

(S3a) $\mathrm{Au}(0)_2 + \mathrm{Au}(0) \xrightarrow{1 mol^{-1} s^{-1}} \mathrm{Au}(0)_3$

(S3b) $\mathrm{Au}(0)_3 + \mathrm{Au}(0) \xrightarrow{1 mol^{-1} s^{-1}} \mathrm{Au}(0)_4 \ldots$

(S3c) $\mathrm{Au(0)_n + Au(0)} \xrightarrow{1 mol^{-1} s^{-1}} \mathrm{Au(0)_{n+1}}$

This step is represented in the simulation:

(S3d) $\mathbf{Au(0)_n + Au(0)} \xrightarrow{1 mol^{-1} s^{-1}} \mathbf{Au(0)_n + Mcount}$

(Seed surface)

(S3e) $\mathrm{Au(0)_{ads} + Au(0)} \xrightarrow{1 mol^{-1} s^{-1}} \mathrm{Au(0)_{ads+1}}$

(S3f) $\mathrm{Au(0)_{ads+1} + Au(0)} \xrightarrow{1 mol^{-1} s^{-1}} \mathrm{Au(0)_{ads+2}} \ldots$

This step is represented in the simulation:

(S3g) $\mathbf{Au(0)_{ads} + Au(0)} \xrightarrow{1 mol^{-1} s^{-1}} \mathbf{Au(0)_{ads} + M'count}$

Symbols $Au(0)_n$ and $Au(0)_{ads}$ represent the gold atoms clusters in solution and on the GNP seeds, respectively. Terms *Mcount* and *M'count* are counting parameters that represent the total number of atoms growing in the solution and on the GNP seeds, respectively. The average cluster size for particles in the solution, N_{sol}, and associated with the seed surface, N_{ads}, are obtained by dividing the total number of atoms by the particle numbers giving the average cluster size:

(S4a) $$N_{sol} = \frac{Mcount}{Au(0)_n}$$

(S4b) $$N_{ads} = \frac{M'count}{Au(0)_{ads}}$$

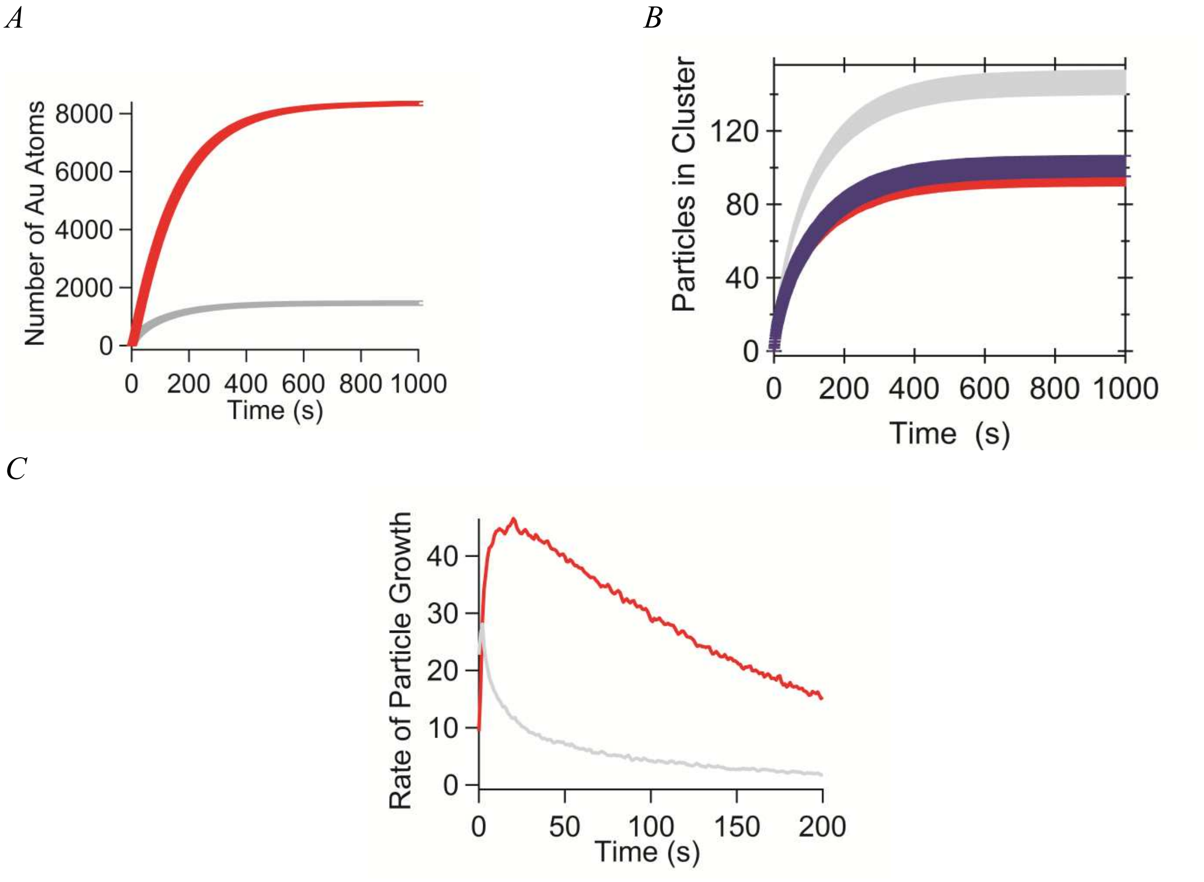

Figure S5. Kinetic Monte-Carlo simulation was used to model the kinetics of seeded and non-seeded species. The figures are an average of 100 runs with Au(III) atoms = 10^4 and seed number being 10, where the variation is represented by ± standard deviation. (A) The number of Au atoms incorporated into new particles in solution over time (red line) and Au atoms that are aggregated to the surfaces of the seeds (grey line). (B) The number of particles in clusters formed in the solution with the seeds (red line) on the seeds (grey line) and when the seeds are not present (blue line). (C) Representative plots of the rate of particle production from Au atoms in solution (red) and the rate of aggregation of Au atoms to seed surfaces (grey).

Derivation of the Kinetic Growth Equation

Assume that the rate of autocatalytic growth is determined by aggregation in the TBP EO/PO blocks on the seed surfaces or in the unimers. Thus:

$2\,Au(0) \xrightarrow{k_1} Au(0)_n$

$Au(0) + Au(0)_n \xrightarrow{k_2} Au(0)_{nm}$

$Au(0) + N_s \xrightarrow{k_3} Au(0)_{ads}$

$Au(0) + Au(0)_{ads} \xrightarrow{k_4} Au(0)_{nm'}$

The rate of aggregative growth is given by

$$R_{gnp} = k_2[Au(0)_n][Au(0)] + k_4[Au(0)_{ads}][Au(0)] \tag{1}$$

Using the steady state approximation:

$$\frac{d[Au(0)_n]}{dt} = k_1[Au(0)]^2 - k_2[Au(0)_n][Au(0)] \approx 0 \tag{2a}$$

$$[Au(0)_n] = \frac{k_1}{k_2}[Au(0)] \tag{2b}$$

$$\frac{d[Au(0)_{ads}]}{dt} = k_3[Au(0)]N_S - k_4[Au(0)_{ads}][Au(0)] \approx 0 \tag{3a}$$

$$[Au(0)_{ads}] = \frac{k_3}{k_4}N_S \tag{3b}$$

Substituting 2b and 3b into equation 1 to obtain equation 4.

$$R_{gnp} = k_1[Au(0)]^2 + k_3[Au(0)]N_S \tag{4}$$

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