Understanding Time-Dependent Surface-Enhanced Raman Scattering from Gold Nanosphere Aggregates using Collision Theory

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Vibrational Mode Assignments for 2-NT. Vibrational mode assignments and frequencies associated with 2-NT are labeled in Figure 3B and summarized in Table S1. The band with the largest intensity occurs at 1067 cm^{-1} and represents a combination band associated with ring breathing, in-plane C-H bending, and ring stretching. This band is representative of signal changes for all observed frequencies and used for evaluating time-dependent changes in SERS spectra.

Table S1. Vibrational mode Assignments for 2-NT

Vibrational Frequency (cm^{-1})	Vibration Mode	Ref.
1449	In-plane C-H bending + Ring CC stretching	1,2
1429	In-plane C-H bending + C-S stretching	1,2
1379	Ring CC stretching	12
1144	In-plane C-H bending	1,2
1130	In-plane C-H bending	1,2
1067	Ring breathing + In-plane C-H bending + Ring stretching	1,2
1022	In-plane C-H bending	2

Modeling Diffusion and Sedimentation Velocities for Au Nanosphere Clusters. Diffusion and sedimentation velocities of clusters are calculated using equations 14 and 15, respectively. These are plotted as a function of cluster size in Figure S1. The net displacement (x) was determined by calculating the average distance between two adjacent nanoparticles in a 5 nM assuming hexagonal packing. A critical cluster size is noted as 325 nm. Clusters with dimensions greater than this value have a probability to sediment out of solution whereas clusters smaller than this value likely do not.

Evaluating Cluster Size as a Function of Nanosphere Concentration using DLS. Time-dependent hydrodynamic diameters of clusters are measured using DLS. In this study, gold nanospheres with a diameter of 13.6 nm and concentrations ranging from 0.5 – 5 nM are incubated with an excess of 2-NT. These data are shown in Figure S2. The self-limiting cluster model (eq. 13) is used to extract rate constants associated with cluster formation. Data in the diffusion-limited regime are analyzed. As nanosphere concentration increases from 0.5 to 5 nM, the rate constant
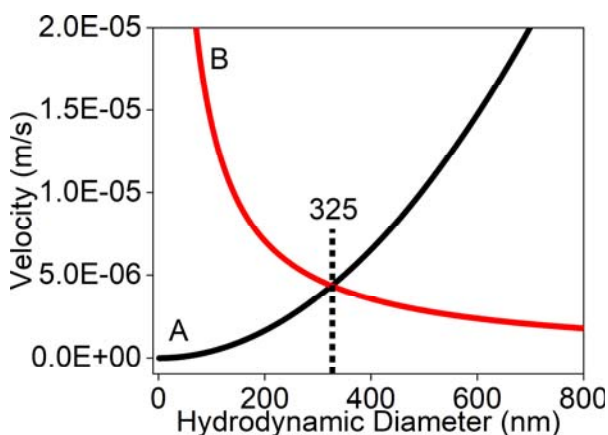

Figure S1. Calculated (A) sedimentation and (B) diffusion velocities for 13.6 nm gold nanospheres. A 5 nM nanosphere concentration suspended in a 5 mM ionic strength aqueous solution at room temperature was used. This result indicates that clusters with hydrodynamic diameters greater than ~325 nm will undergo sedimentation.

associated with cluster formation increases. The number of nanospheres per cluster is calculated using the hydrodynamic diameter of primary nanospheres.

Time-Dependent LSPR, SERS, and DLS as a Function of Nanosphere Diameter. Three-dimensional waterfall plots representing time-dependent LSPR and SERS spectra of 0.5 nM gold nanospheres with diameters ranging from 13.6 - 47.3 nm after the addition of an excess of 2-NT are shown in Figure S3, S4, and S5. DLS data are shown in Figure S6. SERS and LSPR data are plotted with different scale bars so that time dependent trends can be displayed. These data are summarized in terms of flocculation area (from 670-770 nm) and SERS intensity (at 1067 cm^{-1}) in two and three dimensions in Figure S7 and Figure 5, respectively.
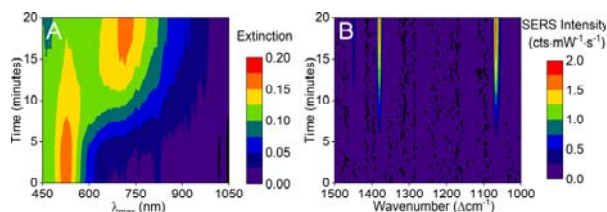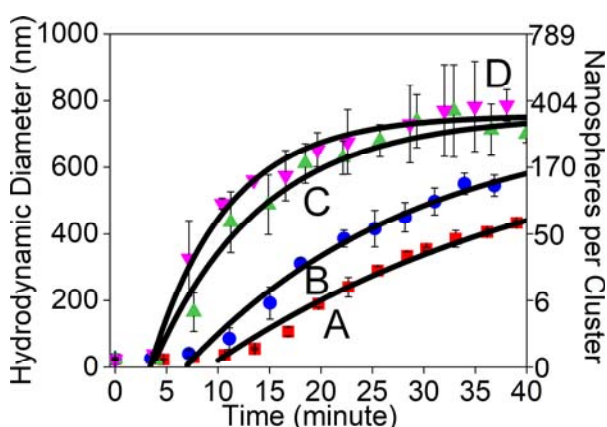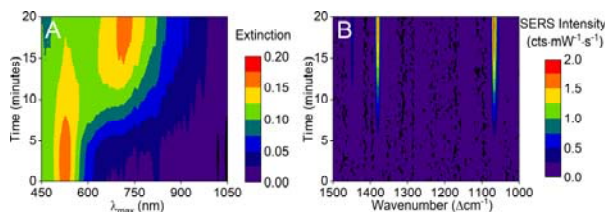

Figure S2. Time-dependent hydrodynamic diameters (left) and (nanospheres per cluster) for clusters resulting from 2-NT addition to (A) 0.5, (B) 1, (C) 3, and (D) 5 nM gold nanospheres (d = 13. 6 nm). Solid black lines are fits using the self-limiting cluster model.

Figure S3. Waterfall maps of time-dependent (A) LSPR and (B) SERS spectra from 0.5 nM gold nanospheres (d=13.6 nm) before and after addition of 2.7 µM 2-NT. Same data collection parameters used in Figure 3 unless noted.

Figure S4. Waterfall maps of time-dependent (A) LSPR and (B) SERS spectra of 0.5 nM gold nanospheres (d=27.7 nm) before and after addition of 11.1 µM 2-NT. Same data collection parameters used in Figure 3 unless noted.
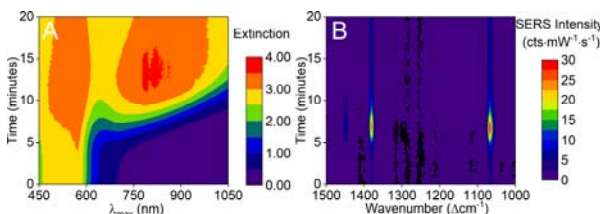

Figure S5. Waterfall maps of time-dependent (A) LSPR and (B) SERS spectra from 0.5 nM gold nanospheres (d=47.3 nm) before and after addition of 32.5 µM 2-NT. Same data collection parameters used in Figure 3 unless noted.
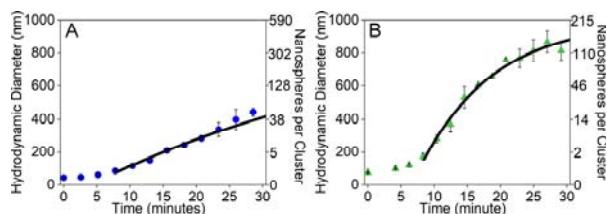

Figure S6. Hydrodynamic diameter of nanoparticles in 0.5 nM gold nanosphere solution with diameters of (A) 27.7 and (B) 47.3 nm. Solid black lines are analyses using the self-limiting cluster model (eq. 13). The number of nanoparticles per cluster is calculated using a packing density of 4.5% and hydrodynamic diameters of primary nanospheres of 42.4 and 59.4 nm for A and B, respectively.
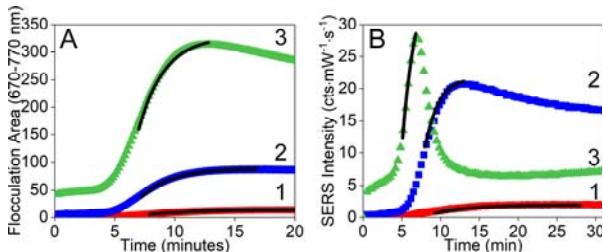
Figure S7. Time-dependent (A) flocculation area calculated from 670-770 nm in LSPR spectra and (B) SERS intensity at 1067 cm^{-1} upon adding an excess of 2-NT to 0.5 nM gold nanospheres with diameters of (1) 13.6, (2) 27.7, and (3) 47.3 nm. Fitted lines represent the self-limited cluster model in the diffusion-limited regime.

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