Supplementary Information (SI) for Nanoscale.

Supporting Information

Plasma-Induced Nanogap Narrowing and Morphological Transformation in Gold Nanoparticle Assemblies

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1. Materials and Methods

1.1 Materials

The following chemicals were purchased and used without further purification to synthesize gold nanoparticles (AuNPs) and assemble them into dimers or core@satellite nanoassemblies:

Gold(III) chloride ($HAuCl_4$, ≥99.9%, Sigma-Aldrich)
Trisodium citrate (≥99.0%, Sigma-Aldrich)
Sodium borohydride ($NaBH_4$, ≥98%, Sigma-Aldrich)
Cetyltrimethylammonium bromide (CTAB, ≥99%, Sigma-Aldrich)
Cetyltrimethylammonium chloride (CTAC, ≥99%, Sigma-Aldrich)
L-ascorbic acid (99%, Sigma-Aldrich)
Sodium bromide (NaBr, ≥99%, Sigma-Aldrich)
Sodium iodide (NaI, ≥99.5%, Sigma-Aldrich)
Silver nitrate ($AgNO_3$, 99.9999%, Sigma-Aldrich)
(3-aminopropyl)trimethoxysilane (APTMS, 97.0%, Sigma-Aldrich)
RBS 35 solution (Sigma-Aldrich)
Sodium oleate (>97%, TCI)
Hydrochloric acid (HCl, 37%, Sigma-Aldrich)
1,8-Octanedithiol (C8DT, 97%, Sigma-Aldrich)
4-aminobenzenethiol (ABT, ≥97.0%, Sigma-Aldrich)
Acetonitrile (CH_3CN, >99.5%, Daejung Chemicals, Korea)
Ethanol (≥99.9%, Duksan Chemical, Korea)
Ultrapure water (HPLC grade, J. T. Baker)

The following instruments were used to measure the properties of AuNPs and assemble them into nanoassemblies:

UV–vis spectrometer (Lambda 25 or Lambda 365+, PerkinElmer, U.S.A)
Transmission electron microscope (TEM, JEM-F200, JEOL, Japan)
Scanning electron microscope (SEM, Sigma, Carl Zeiss, Germany)
Rotator mixer (KRM-5, Korea Bio-Tech, Korea)
Syringe pump (NE-300, New Era, U.S.A)
Plasma cleaner (PDC-32G-2, Harrick Plasma, U.S.A)
Raman spectrometer (Leica DM + RamanRxn1, Kaiser Optical Systems, U.S.A)
Laser (785 nm LM-785, Ondax, U.S.A)

1.2 Nanoparticle Synthesis

A. Synthesis of Gold Nanospheres (AuNSs)

Citrate-capped AuNSs with a diameter of 18 nm were synthesized using the Turkevich method.[1] Specifically, 990 mL of 1.7 mM trisodium citrate solution was heated up to 100℃ while being vigorously stirred in a three-necked round-bottom flask in a heating mantle. Then, 5 mL of 51 mM gold(III) chloride solution was injected into the flask. Boiling and stirring were continued for 30 min.

Larger AuNSs with diameters of 23, 55, 67 nm were prepared using the seed-mediated synthesis method developed by Puntes and coworkers, with slight modifications.[2] Specific input volumes of

reagents for each reaction step are summarized in **Table S1**. A 60 mM trisodium citrate solution and a 25 mM gold(III) chloride solution were used in all steps. This method involves the following steps:

Step 1: Gold seeds were synthesized by boiling a mixture of trisodium citrate solution and water with vigorous stirring. Gold(III) chloride solution was then injected into the boiling solution. The reaction proceeded for 30 min, after which the solution was cooled to 90 °C.

Step 2: Gold(III) chloride solution was injected into the seed solution. After 30 min, gold(III) chloride solution was injected once more. The solution was allowed to react for an additional 30 min.

Step 3: Water was added to the solution from the previous step. Once the solution reached 90 °C again, trisodium citrate solution was added. Subsequently, gold(III) chloride solution was injected into the solution twice, with a 30 min interval between injections. The solution was allowed to react for 30 min. Step 3 was repeated until an extinction peak appeared at the desired wavelength.

Table S1. Sequence and amounts of added reagents for the synthesis of AuNSs using the seed-mediated growth method.

Step	Reagent	$AuNS_{23}$	$AuNS_{55}$	$AuNS_{67}$
		Amount (mL)		
1	Water	600	144.5	144.5
	Trisodium citrate	24	5.5	5.5
	Gold(III) Chloride	4	1	1
2	Gold(III) Chloride	4 + 4	1 + 1	1 + 1
3	Water		144	141
	Trisodium citrate		4	6
	Gold(III) Chloride		2 + 2	3 + 3
4	Water		135	141
	Trisodium citrate		10	6
	Gold(III) Chloride		5 + 5	3 + 3
5	Water		285	168
	Trisodium citrate		10	6
	Gold(III) Chloride		5 + 5	3 + 3
6	Water			0
	Trisodium citrate			10
	Gold(III) Chloride			5 + 5
7	Water			0
	Trisodium citrate			12
	Gold(III) Chloride			6 + 6

B. Synthesis of Gold Nanocubes (AuNCs)

CTAC-capped AuNCs were synthesized using the method developed by Nam and his coworkers.[3] All reactions were conducted in a water bath (30 °C). First, CTAB-capped gold clusters were prepared by adding 0.25 mL of 10 mM gold(III) chloride solution to 9.75 mL of 100 mM CTAB solution. Next, 0.6 mL of ice-cold 10 mM sodium borohydride solution was rapidly added to the mixture. The mixed solution was stirred for 3 min and then left undisturbed for 3 h. CTAC-capped gold nanoparticle seeds were grown from the clusters obtained in the previous step. A mixture of 2 mL of 200 mM CTAC, 1.5 mL of 100 mM L-ascorbic acid, and 0.05 mL of the cluster solution was prepared and stirred. While stirring, 2 mL of 0.5 mM gold chloride(III) solution was injected into the mixture. Stirring continued for 15 min at room

temperature. The seed solution was then purified by centrifugation at 17000 rpm for 1 h and redispersed in 10 mL of 20 mM CTAC solution.

For the synthesis of AuNCs, a mixture of 1.5 mL of 10 mM gold(III) chloride solution, 15 mL of 200 mM CTAC solution, 1.02 mL of ascorbic acid solution, 0.3 mL of 10 mM sodium bromide solution, and 42.45 mL of water was prepared. Subsequently, 0.034 mL of seed solution was injected into the mixture solution. The entire mixture was gently shaken and then left undisturbed for 30 min. The resulting AuNCs solution was centrifuged twice (4500 rpm, 10 min) and redispersed in water.

C. Synthesis of Gold Nanorods (AuNRs)

CTAB-capped AuNRs were synthesized using the method reported by Murray and coworkers, with slight modification.[4] For the synthesis of CTAB-capped seeds, 5 mL of 0.5 mM gold(III) chloride solution and 5 mL of 200 mM CTAB solution were mixed. Then, 0.6 mL of 10 mM sodium borohydride solution was added to the mixed solution under vigorous stirring. After 2 min, the solution was left undisturbed for 2 h in a water bath at 30 °C.

For the synthesis of AuNRs, 0.7 g of CTAB and 0.1234 g of sodium oleate were each dissolved in 12.5 mL warm water (70 °C). The dissolved solutions were mixed and cooled down to 30 °C. Then, 1.2 mL of 4 mM silver nitrate solution was added, and the mixture was left undisturbed for 15 min at 30 °C. Subsequently, 2.5 mL of 10 mM gold(III) chloride solution and 22.5 mL of water were added to the solution. The solution was stirred for 90 min. After the solution became colorless, 0.21 mL of hydrochloric acid was added, and the mixture was stirred for 15 min. Thereafter, 0.125 mL of 64 mM L-ascorbic acid and 80 µL of the seed solution were added to the stirring solution at intervals of 30 s, then it was left undisturbed for 12 h. For purification, the resulting AuNR solution was centrifuged (first at 7000 rpm for 30 min, then at 5500 rpm for 20 min) and redispersed in pure water.

D. Synthesis of Gold Nanotriangles (AuNTs)

CTAC-capped AuNTs were synthesized using the same method as in our previous paper.[5, 6] CTAC-capped seeds were initially prepared by the following steps: (1) 0.025 mL of 50 mM gold(III) chloride solution and 4.7 mL of 100 mM CTAC solution were mixed. (2) 0.3 mL of 10 mM sodium borohydride solution was swiftly injected into the mixture, while stirring continued for 2 h. (3) Subsequently, 0.5 mL of the seed solution was diluted with 4.5 mL of 100 mM CTAC solution.

Two separate solutions, labeled A and B, were prepared in different vials:

Solution A: 1.6 mL of 100 mM CTAC solution, 8 mL of water, 0.04 mL of 50 mM gold(III) chloride solution , and 0.015 mL of 10 mM sodium iodide solution

Solution B: 20 mL of 100 mM CTAC solution, 20 mL of water, 0.5 mL of 50 mM gold(III) chloride solution, and 0.3 mL of 10 mM sodium iodide solution.

0.04 mL of 100 mM L-ascorbic acid solution was added to solution A, while solution B received ten times the volume of 100 mM L-ascorbic acid solution compared to solution A. Both solutions were gently shaken until they turned colorless.

0.1 mL of the diluted seed solution was injected to solution A, and the mixture was slightly shaken. Immediately afterward, 3.2 mL of solution A was transferred to solution B. The reaction proceeded for 1 h under stirring and then underwent centrifugation (6000 rpm, 20 min) once. The resulting precipitate was redispersed in 20 mL of 150 mM CTAC and left undisturbed for 16 h. AuNTs precipitated at the bottom of the vial, so the supernatant was removed using a pipette. Finally, 20 mL of water was added to disperse the precipitated AuNTs.

E. Synthesis of Perfect Sphere AuNSs

CTAC-capped perfect AuNSs were synthesized using a slightly modified method developed by Xia and coworkers.[7] The reactions were carried out in a warm water bath at 30 °C. First, CTAB-capped gold clusters were prepared by mixing 0.25 mL of 10 mM gold(III) chloride solution with 5 mL of 200 mM CTAB solution and 4.75 mL of water, under moderate stirring. Then, 0.6 mL of 10 mM sodium borohydride solution was injected into the mixture. The mixture was stirred for 1 min and then left undisturbed for 30 min.

CTAC-capped gold nanoparticle seeds were synthesized from the clusters obtained in the previous step. A mixture with the same composition as that used in the cube synthesis process was prepared and stirred. While stirring, 2 mL of 1 mM gold(III) chloride solution was added. The mixture was left undisturbed for 30 min, followed by centrifugation at 17,000 rpm for 1 h. The supernatant was removed, and the precipitate was redispersed in 5 mL of water.

For the synthesis of AuNSs, a mixture of 30 mL of 200 mM CTAC, 24.4 mL of water, 3.6 mL of 10 mM ascorbic acid, and 0.4 mL of the seeds was prepared under mild stirring. Subsequently, 15 mM gold(III) chloride solution was injected into the mixture at a rate of 2 mL/h for 1 h using a syringe pump. After the injection was completed, the mixture was stirred for an additional 30 min, followed by centrifugation at 10,000 rpm for 15 min and redispersion in water.

1.3 Characterization Data of Synthesized AuNPs

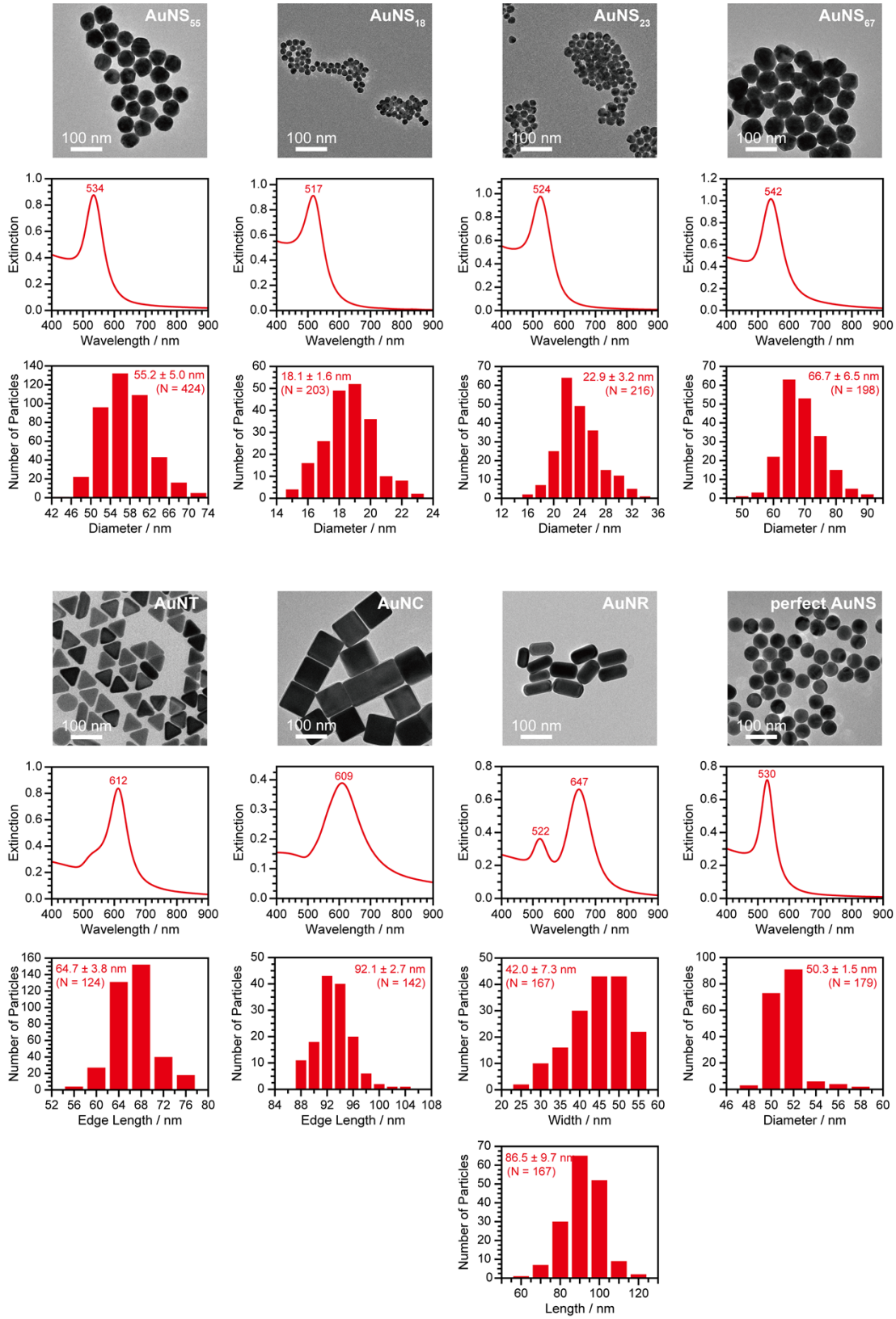

Figure S1. (a) Representative TEM images (b) UV–vis spectra, and (c) size distribution of the AuNPs used in this study.

1.4 Nanoparticle Assembly

Figure 1 illustrates the assembly method of AuNS homodimers. Below, we provide more detailed information on the entire assembly process:

***Step 1*:** A glass slide (Marienfeld, Germany) was cut to a size of 2.5 cm × 1.3 cm and cleaned using RBS solutions at 90 °C for 5 min. The glass slide was then amine-functionalized by immersing it in 1% v/v APTMS ethanolic solution for 30 min. It was subsequently transferred to an ethanol-containing tube and sonicated for 5 min. After rinsing with ethanol and drying with nitrogen gas, the glass slide was placed in an oven at 125°C for 30 min.

***Step 2*:** The amine-functionalized glass slide was immersed in a "first" (or "core") AuNP solution for 20–30 min to adsorb the negatively surface-charged AuNPs while being rotated in a rotator mixer. The first AuNPs include citrate-capped AuNSs in water or CTAC-capped AuNPs (AuNCs, AuNRs, and AuNTs) in an aqueous solution of 90% v/v acetonitrile.[8] The glass slide was washed with ethanol and dried with nitrogen gas after adsorption.

***Step 3*:** The surfactants (citrate, CTA) on the AuNPs were removed through RF plasma treatment (18 W, 90 s) with ambient air under 0.8 Torr pressure. This step also removes the unbound amine coating from the glass substrate. After the plasma treatment, the AuNP/glass substrate was washed with water and ethanol.

***Step 4*:** The AuNPs from previous step were functionalized by immersing the substrate in an ethanolic solution of linker (C8DT or ABT). In this step, linker molecules were attached to the bare surfaces of AuNPs. After 1 h, the functionalized AuNP/glass substrate was rinsed with ethanol.

***Step 5*:** The linker-attached AuNP/glass substrate was immersed in a "second" (or "satellite") AuNP solution. The immersion methods for dimers and core-satellite assemblies differ slightly. For dimers, the substrate was incubated in the AuNP solution undisturbed for 8 h. To assemble the core-satellite structures, the substrate was rotated in a rotator mixer for 2 h. The substrate was rinsed with ethanol after assembly process was completed.

1.5 Plasma Treatment

Plasma was applied to the AuNP assemblies on the glass substrate to progressively narrow the nanogaps within the assemblies. The AuNP assemblies on the glass substrate were dried with nitrogen gas and then placed in a plasma cleaner. The pressure inside the plasma cleaner was set to 0.8 Torr, and plasma was applied to the sample at 18 W for 1 min. After each treatment, the sample was removed from the cleaner, and its characteristics were immediately measured using UV–vis and/or Raman spectroscopy. This sequence was repeated, resulting in a total plasma treatment time of 15 min for the measurements in Figure 2c and 10 min for Figures 3b and 3c.

1.6 Measurements

Detailed information about the instruments used to measure the characteristics and properties of AuNPs and their assemblies is provided in **Section 1.1**. The structures of the AuNP building blocks and their assemblies were determined by transmission electron microscopy (TEM) and scanning electron microscopy (SEM), respectively. Optical properties, such as extinction, were measured using UV-vis spectroscopy. Extinction spectra of AuNPs and their assemblies on glass substrates were obtained by placing the sample diagonally in a quartz cuvette.

To acquire Raman spectra, the nanoassemblies on glass substrates were placed on the microscope stage and a 785 nm laser was directed onto the sample through an objective lens (50x, N.A. 0.75, Leica). The Raman scattered light was collected using the same objective and transmitted to a spectrometer equipped with a transmissive holographic grating and a CCD detector. The laser power was set to 1 mW, and the focus size was 20 μm.

1.7 Simulations

Absorption and scattering spectra of the core-satellite nanoassemblies were calculated using the finite-difference time-domain (FDTD) method. The constructed model matched the experimental size but featured improved symmetry. The gap distances between the core AuNS and the satellite AuNSs were set to 1.3 nm, corresponding to the distance of the C8DT linker. Johnson and Christy values were employed for the dielectric function of gold.[9] A total field-scattered field (TFSF) source (λ = 400–900 nm) propagated from the top of the model, exciting the plasmon of the nanoassembly with polarization along the core and satellites on the side. The simulation region was enclosed by perfectly matched layer (PML) boundaries, with dimensions of 1500 nm × 1500 nm × 1500 nm and a background index of 1.33. The calculation mesh size was set to 0.5 nm. Absorption and scattering cross-section monitors were placed inside and outside the source boundaries, respectively. The simulation time was set to 1000 fs, with an automatic shut-off level at 10^{-8} s.

2. Characterization of AuNS Dimers

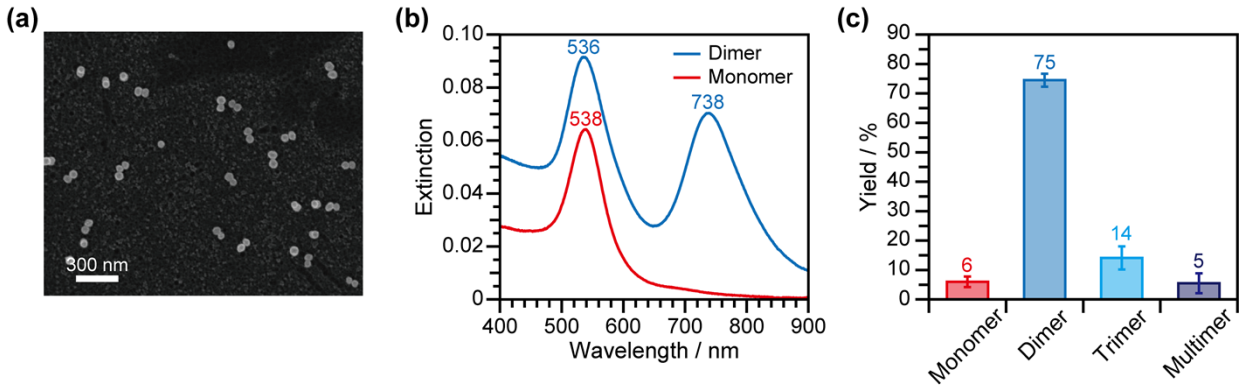

Figure S2. Characterization of AuNS dimers assembled on a glass slide. (a) Representative SEM image of AuNS dimers. (b) UV–vis extinction spectrum of the AuNS dimers on a glass slide (blue line) compared with that of the monomeric AuNSs before assembly (red line). Note that these spectra were obtained with the sample immersed in ethanol. The peak positions change sensitively with the surrounding medium; for instance, the peaks at 536 and 738 nm for the dimers shift to 515 and 695 nm in air, as shown in Figure 2c. (c) Population distribution of the AuNS assemblies on the glass slide, showing that dimers make up 75% of the total particles (*N* = 5192).

3. SERS Spectra of AuNS Dimers with ABT Linkers after Plasma Treatment

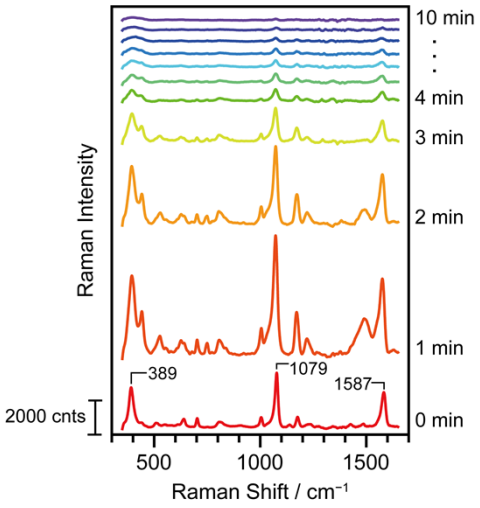

Figure S3. Raman spectra of AuNS dimers with ABT linkers, obtained after plasma treatment for the indicated time durations. Baselines were subtracted, and the spectra have been offset for clarity.

4. TEM Images of Perfect Sphere AuNSs After Plasma Treatment

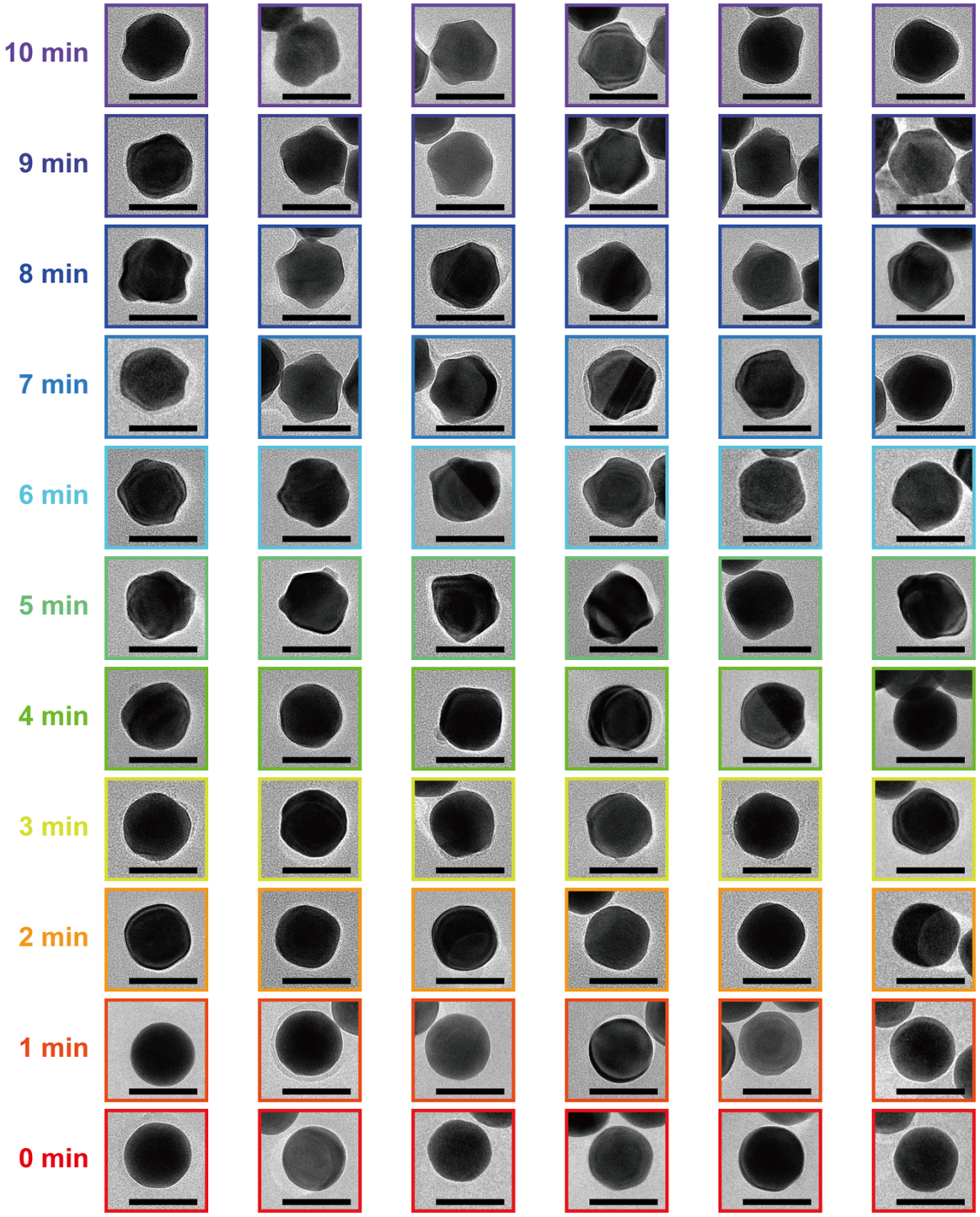

Figure S4. Collection of TEM images of perfect sphere AuNSs prepared on glass substrates, following the steps up to (d) in Figure 1. The AuNSs were then treated with plasma (air, 0.8 Torr, RF power: 18 W) for the specified durations. Scale bars represent 50 nm.

5. References

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