Polyhedral plasmonic nanoclusters through multi-step colloidal chemistry – Supplementary Information

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1. Experimental Methods

Note: All chemical procedures described below must be performed in a fume hood. Researchers must wear appropriate personal protective equipment (PPE), including lab coat, gloves, and safety glasses or goggles.

1.1. Synthesis of surface-functionalized spherical silica particles.

1.1.1. Synthesis of spherical silica particles. We use a two-stage protocol [1, 2] to synthesize silica particles. The first stage is the synthesis of pre-seeds. We pour 100 mL of 6 mM L-arginine aqueous solution (purchased from Sigma-Aldrich, 99%) in a 150 mL double-walled vial equipped with a reflux condenser. When the temperature stabilizes at 60 °C, we add 10 mL tetraethoxysilane (TEOS, Sigma-Aldrich 99%). We set the magnetic stirring to 150 rpm for a 3 cm cylindrical magnetic stirrer to generate a small and stable vortex and an interface of constant surface area between both phases. The reaction continues until the TEOS (upper phase) fully disappears, typically in two days. We estimate the diameter of the as-obtained silica pre-seeds from TEM imaging and find an average value of 29.2 nm and a polydispersity index (PDI) of 1.01. The dry extract method allows us to determine the silica concentration $(25.2 \,\mathrm{g \, L^{-1}})$ and then to calculate the concentration of preseeds $(8.8 \times 10^{-17} \,\mathrm{L}^{-1})$. In the second stage, we re-grow these silica pre-seeds in a 1L flask surmounted by a bubbler where 455 mL ethanol (Sigma-Aldrich), 35 mL ammonia (J.T. Baker, 28-30% in water) and $10\,\mathrm{mL}$ pre-seed aqueous dispersion are mixed by magnetic stirring. Then the proper volume of TEOS is added dropwise using a syringe pump at the rate of $0.5\,\mathrm{mL}\,\mathrm{h}^{-1}$ to reach a TEOS/silica weight ratio of 83. In such conditions, the diameter of the silica particles increases to 86 nm (PDI = 1.002) and the final concentration of the silica particles is $1.47 \times 10^{-16} L^{-1}$.

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To achieve 137 nm silica particles (PDI = 1.001), we use this last silica particle dispersion and add TEOS dropwise again to reach a TEOS/silica weight ratio of 20.

1.1.2. Functionalization of silica particles with carboxylic acid groups. We modify the 137 nm silica particle surfaces with amino groups and then derivatize into carboxylic ones following a previously reported protocol [3]. We carry out the reaction just after the regrowth stage, in the same reacting medium, where we add an amount of APTES (aminopropyltriethoxysilane, Sigma-Aldrich, 98%) corresponding to 20 functional groups per nm² of silica surface. We stir the dispersion for 12 h at room temperature. Then we add a volume of glycerol (Sigma-Aldrich, 99%) corresponding to 10% of the dispersion volume. We evaporate ethanol and water using a rotary evaporator set at 90 °C. We heat the dispersion in glycerol, in an oil bath set at 105 °C for a subsequent 2 h thermal treatment under the vacuum produced by a rotary vane pump (RV5 from Edwards). Finally, we wash the particles by performing four cycles of centrifugation/redispersion in ethanol (12,000g for 20 min). We check the efficiency of the reaction by ζ -potential measurements performed in water, which show a value of $(+35 \pm 3)$ mV in the 4–10 pH range.

Next, we transfer the aminated silica particles to dimethylformamide (DMF) by performing three centrifugation/redispersion cycles (12,000q for 20 min). Between the second and third cycle, we add an amount of triethylamine (TEA, Sigma-Aldrich, 99.5%) corresponding to 50 functional groups per nm² of silica surface. We adjust the volume to 50 mL and transfer the dispersion into a round-bottom flask placed in an oil bath set at 60 °C for dehydration for 2 h under the vacuum of the rotary vane pump. We add an amount of succinic anhydride (Sigma-Aldrich, >99%) corresponding to 50 functional groups per nm² of silica surface and let react overnight at 60 °C. We wash the particles by two centrifugation/redispersion cycles in ethanol and three extra ones in DMF (12,000g for 20 min). We add an amount of TEA corresponding to 50 functional groups per nm^2 before the last washing cycle, and we dehydrate the last dispersion under the vacuum of the rotary vane pump. We check the efficiency of the reaction by ζ -potential measurements performed in water, which show a value of $(+35 \pm 5)$ mV in the 5–10 pH range, and by infrared absorption spectroscopy, which shows the presence of amide and carboxylate groups in stretching bands at $1650 \,\mathrm{cm}^{-1}$ and $1730 \,\mathrm{cm}^{-1}$, respectively.

1.2. Synthesis of aminated dimpled silica particles.

1.2.1. Synthesis of dimpled silica particles from silica/polystyrene octahedra. We prepare batches of silica/polystyrene octahedra made of a central 86 nm silica core and six polystyrene (PS) satellite nodules by seeded-growth emulsion polymerization of styrene, according to a previously developed procedure [2, 4]. Briefly, this procedure consists of the emulsion polymerization of styrene performed in the presence of the 86 nm silica particles, which are surface modified with methacryl-oxymethyltriethoxysilane (MMS, ABCR, 98%).

The MMS modification reaction is carried out just after the silica regrowth stage, in the same reacting medium, where we add an amount of MMS corresponding to 0.5 functional groups per nm² of silica surface. We let react under stirring for 3 h at room temperature before heating to 90 °C for 1 h under reflux of ethanol. We concentrate the dispersion with the rotary evaporator to remove ethanol and ammonia and replace them with water. Then we let the dispersion cool down

Number of PS satellites	% of clusters
1	0
2	0
3	7
4	13
5	18
6	62
7 or more	0

TABLE S1. Distribution ($N \approx 100$) of cluster morphologies after synthesis of silica cores with polystyrene satellites.

at room temperature and dialyze against water for three days. We measure the particle concentration by the dried extract method.

In a 250 mL three-neck flask, equipped with a stirring anchor and a condenser surmounted by a bubbler, we introduce water, the 86 nm silica seed dispersion $(7.3 \times 10^{15} \text{ L}^{-1})$, and a surfactant mixture (3 g L^{-1}) made of Symperonic NP30 (95% w/w) and sodium dodecylsulfate (SDS, Sigma-Aldrich, >90%, 5% w/w). We thoroughly deaerate the dispersion by bubbling nitrogen through it while stirring (170 rpm). We emulsify by adding styrene (Sigma-Aldrich, 99%, 100 g L⁻¹) at 250 rpm for 15 min. We carry out the polymerization at 70 °C after addition of sodium persulfate (Sigma-Aldrich, 99%, 0.5% w/w with respect to styrene). After 6 h, the monomer-to-polymer conversion is 80% as determined by the dried extract method. We characterize the sample by TEM and determine statistically that it consists of octahedra with a morphology yield of 62% (Table S1). The average diameter of the PS satellites is 150 nm.

We overgrow the silica cores using a previously reported method [5]. We prepare a mixture of 450 mL ethanol and 35 mL ammonia (1 M) and first add a volume of the polymerization medium to fix the octahedron concentration to $1.5 \times 10^{14} \,\mathrm{L^{-1}}$. Then we add 4.5 mL TEOS ($10 \% \,\mathrm{v/v}$ in ethanol) at a rate of 1 mL h⁻¹. We make the silica surface hydrophobic by adding a volume of propyltrimethoxysilane (PTMS, Sigma-Aldrich, >98 %) corresponding to 50 functional groups per nm² of the silica surface area. We complete the reaction under stirring at ambient temperature for 12 h. Finally, we wash the particles by performing three cycles of centrifugation (12,000g for 20 min) and redispersion in ethanol. TEM experiments show that the diameter of the silica core increases from 86 nm to 145 nm.

To dissolve the PS satellites, we add a volume of DMF equal to 10% of the total volume. Subsequently we heat the dispersion to 70 °C and partially evaporate it under vacuum using a rotary evaporator. Then we increase the temperature to 90 °C and let the evaporation continue until the dispersion changes from white to almost transparent. To remove the dissolved PS, we perform three cycles of centrifugation/redispersion in THF (10,000g for 20 min). From analysis of the TEM images, we find that the yield of silica cores with six dimples is 60% (Table S2).

1.2.2. Amination of the residual PS macromolecules at the bottom of the dimples. For this procedure, we use a previously reported recipe [6]. Briefly, after transferring the as-prepared dimpled silica particles in chloroform, we add butyl chloromethyl ether in chloroform (3 M; 5 mL) and 0.3 mL tin tetrachloride (SnCl₄, Sigma-Aldrich, >99%). We set the temperature to 45 °C and then age the mixture overnight.

Number of dimples	% of particles
1	0
2	0
3	1
4	12
5	27
6	60
7 or more	0

4

TABLE S2. Distribution $(N \approx 100)$ of silica core morphologies after silica regrowth and dissolution of the PS satellites.

Finally we wash the nanoparticles using three cycles of centrifugation/redispersion (5,000g for 15 min) in aqueous HCl solution (4% w/w) and then in water/ethanol (50/50 w/w) before redispersion in 20 mL DMF. We perform the amination using 10^{13} chloromethylated silica particles in DMF and 3 mL ethylene diamine (Fluka, 99.5%), such that the ethylene diamine is in excess to minimize cross-linking. We heat the system to 90 °C and let the reaction proceed overnight under stirring. We wash the nanoparticles using two cycles of centrifugation/redispersion (12,000g for 20 min) in ethanol and two additional cycles in water. After having protonated the amino groups with a few drops of HCl, we centrifuge the dispersion and redisperse the particles in water. Lastly, we transfer the aminated dimpled silica particles into DMF by performing two cycles of centrifugation/redispersion (12,000g for 20 min). We add an amount of TEA corresponding to 50 functional groups per nm² of surface of a sphere of similar diameter and we wash the solution one more time with DMF. Finally, we remove the remaining water from the dispersion by heating at 50 °C under stirring and vacuum generated by a rotary vane pump for 1 h.

1.3. Synthesis of silica/silica octahedra. To assemble the 137 nm carboxylated spherical silica particles onto the 145 nm aminated dimpled silica particles, we use a peptidic coupling reaction. We perform the reaction in DMF, activating the carboxylate groups with ethyl chloroformate (ECF, Sigma-Aldrich, >97%) used in exact stoichiometry, avoiding thoroughly the presence of water, and efficiently deprotonating the reactive groups with triethylamine (TEA). In a 1.5 mL Eppendorf tube, we introduce the DMF dispersion of carboxylated silica particles and an amount of ECF corresponding to 4 functional groups per nm^2 of silica surface, mix on a vortexer, and homogenize on a roller mixer for 2 min. Then we add the DMF dispersion of aminated dimpled silica particles in excess, such that there are 400 carboxylated particles for each aminated dimpled ones, and we let the assembly proceed for 30 min on the roller mixer. We transfer the dispersion to 40 mL water (containing 0.1 mL TEA) and attempt to selectively remove the excess of carboxylated particles by performing three centrifugation/redispersion cycles (500gfor 20 min). We check the assembly success and silica/silica octahedron morphology by TEM.

1.4. Gold decoration of silica satellites of the silica/silica octahedra. We grow a gold shell specifically onto the silica satellites by first turning the carboxylate groups into amino ones, then adsorbing tiny gold nanoparticles (diameter of 2 nm to 5 nm prepared by following a previously developed recipe [7]) selectively on

the satellites. A gold plating solution (GPS) prepared according to a previously reported protocol [8] is then used to grow a gold shell on the gold-seed-covered satellites.

Because the carboxylate groups are deactivated at the time of the purification step in water, we re-activate them by transferring them into DMF and adding ECF under conditions previously described. After 5 min, we add an amount of ethylene diamine corresponding to 50 functional groups per nm² of the silica satellite surface and let the mixture react overnight. Then we wash the particles by three centrifugation/redispersion cycles in water (2,000g for 10 min), acidify using a few drops of HCl (CAUTION: strong acid; wear face shield, gloves, lab coat, and other appropriate PPE) to protonate the amino groups, and wash one more time with water.

In parallel, we prepare the tiny gold seeds in a 500 mL flask by introducing 227.5 mL water, 7.5 mL aqueous solution of NaOH (Sigma-Aldrich, 98%, 0.2 M) and 5 mL tetrakis(hydroxymethyl)phosphonium chloride (THPC, Aldrich, 80%) aqueous solution (120 μ L in 10 mL). After homogenization for 15 min under stirring, we quickly inject 10 mL HAuCl₄ (25 mM, Sigma-Aldrich, 99.9%). The solution turns from pale yellow to brown in a few seconds, indicating the formation of gold nanoparticles.

We put these tiny gold nanoparticles (30 mL) in contact with the silica/silica octahedra (1 mL) by mixing both dispersions, and we let the selective adsorption proceed over a roller mixer for at least 4 h. We wash the particles and remove excess gold seeds by three centrifugation/redispersion cycles in water (500g for 20 min).

To make the GPS, we prepare a 10 mL stock solution of gold precursor from HAuCl₄ (25 mM) and store it in the dark at 4 °C. In a 100 mL flask, we mix 8 mL gold stock solution and 300 mg potassium carbonate and then fill the flask to a total volume of 100 mL with water. We stir the solution overnight at 4 °C.

In a 50 mL falcon tube, we introduce the gold decorated silica/silica octahedra (0.5 mL), PVP solution $(10 \text{ mL}, 10 \text{ g L}^{-1})$, the GPS solution (25 mL), and formaldehyde (1.25 mL). We let the reaction proceed for at least 12 h over a roller mixer. Then we wash the nanoparticles using three cycles of centrifugation (3,000g for 15 min) and redispersion in water. To tune the gold shell thickness, we vary the amount of GPS solution (X mL) and formaldehyde (X/20 mL) where X is the value of the targeted shell thickness in nanometers. We vary the value of X from 5 to 35 to achieve clusters with different shell thicknesses as shown in Fig. 2a on main text. At 25 mL of GPS solution, we estimate the yield of octahedral clusters with gold shells to be 60% (Table S3) from TEM image analysis.

For reference, TEM images and an extinction spectrum of gold nanoshells produced using the same seeded-growth protocol are shown in Fig. S5.

1.5. Characterization techniques.

1.5.1. Transmission electron microscopy (TEM). We perform TEM measurements using a Philips CM20 microscope that operates at 75 kV. We prepare the samples by depositing one drop of the colloidal dispersion on a conventional carbon-coated copper grid. We then air-dry the grids at room temperature and store in a closed box to prevent dust accumulation.

1.5.2. Scanning transmission electron microscopy (STEM). We perform STEM measurements coupled with energy dispersive X-ray spectroscopy (EDX) using a JEOL

Number of gold nanoshell satellites % of clusters

4	12
5	28
6	60

TABLE S3. Distribution (N = 30) of cluster morphologies after gold nanoshell growth on silica satellites. We count only 4-, 5-, and 6-particle clusters that contain a silica core particle. We do not count aggregates of particles that are seen on the TEM grid (see Fig. 1b of the main text). These aggregates consist of unattached gold nanoshells and likely result from drying forces during TEM sample preparation, as explained in the caption of Fig. 1.

2200 FS equipped with a field emission gun which operates at 200 kV (PLACAMAT, UMS 3626 CNRS/Univ. Bordeaux). STEM-EDX images are shown in Fig. 1c.

1.5.3. Single-cluster dark-field spectroscopy. To prepare a sample for single-cluster spectroscopy, we mix a dispersion of 10 μ L of the gold-decorated octahedra with 450 μ L of ultrapure deionized water (obtained from a Millipore Synthesis) in an Eppendorf tube. We homogenize the dispersion using a vortexer and an ultrasonic bath. We deposit 3 μ L of this suspension on a TEM grid (Electron Microscopy Sciences, model number LF200) and let it dry. The TEM grids contain squares with distinct alphabetical markers and are covered with a thin layer of Formvar, a hydrophobic polymer. After drying the suspension on the grid, we observe the sample with a FEI Tecnai F20 Cryo-Bio 200kV TEM. We identify the locations of isolated octahedral clusters using the alphabetical markers on the TEM grid and by taking micrographs at a range of magnifications. Finally, we transfer the grids to the spectroscopy setup.

In the dark-field setup, we use an unpolarized white light beam from a halogen goose neck lamp (supplied by Cole Parmer, 41723-Series high intensity illuminator). We focus the beam on the sample using a $20 \times \log$ working distance Olympus objective. The incidence angle of light is about 65° with respect to the direction perpendicular to the sample. This oblique incidence angle ensures that only the scattered light passes through the collection objective. We mount the sample on a rotation stage which is placed on a motorized stage connected to the microscope-spectrometer setup (LabRAM HR Evolution Raman spectrometer from HORIBA Scientific). We collect scattered light from the sample using a $50 \times \log$ working distance Olympus objective with a numerical aperture of 0.5. We use an adjustable aperture situated in the optical path of the spectrometer to collect scattered light from only the surroundings of one cluster, with an area of approximately 1 μ m².

We measure the spectrum of scattered light from individual clusters by subtracting the signal from the background and then normalizing by the incident light spectrum:

(S1)
$$I = \frac{I_{\rm sc} - I_{\rm bg}}{I_{\rm inc}}$$

where $I_{\rm sc}$ is the measured intensity of the scattered light *with* a cluster in the field of view and $I_{\rm bg}$ is the measured intensity of the scattered light *without* a cluster.



FIGURE S1. Views of the simulation setup, as output by Lumerical. (a) 3D view of setup for *p*-polarized light. (b) Sideview of setup for *p*-polarized light. (c) 3D view of setup for *s*-polarized light. (d) Sideview of setup for *s*-polarized light.

 $I_{\rm inc}$ is the intensity of incident light recorded from a Spectralon diffuse reflectance standard (supplied by Labsphere).

2. Simulation methods

We use the commercial package Lumerical to perform finite-difference timedomain (FDTD) simulations of scattering from the nanoclusters. We use a totalfield-scattered-field implementation, which allows us to separate the scattered field from the incident field. We model a cluster by implementing the octahedral geometry with the approximate parameters measured from TEM images. To replicate the experimental setup, we place the cluster on a substrate (thickness 30 nm, refractive index 1.5) and implement an incidence angle of 25°. The simulation setup is shown in Fig. S1. Fig. S2 shows a cross-sectional view and the mapping of refractive index across the model of the cluster. It shows the presence of the gold shells surrounding spherical silica particles. From simulations, we measure the scattered light at coordinates in the far-field, a centimeter away from the cluster (approximately the distance between the cluster and objective lens in experiment). We implement the numerical aperture by defining a cone with an opening angle of 30° and integrating the scattered light intensity over the area of the base of the cone. To measure the



FIGURE S2. Map of refractive index in a cross-sectional plane of an octahedral nanocluster, as output by Lumerical.

response to our unpolarized light source, we perform simulations separately with s-polarized and p-polarized incident light and take their sum (Fig. S3). To plot the far-field radiation patterns as shown in Fig. S4, we calculate the intensity of scattered light along the perimeter of a circle with a diameter of 1 m placed in three different planes: the XY, YZ, and XZ planes.



FIGURE S3. Scattering spectra for clusters with different gaps. The total intensity is the sum of the intensity of *s*-polarized and *p*-polarized light. We find one dominant peak for each of the polarizations. For a 1.98 nm gap geometry, the peak for *s*-polarized light is around 770 nm and the peak for *p*-polarized light is around 892.5 nm. As the gap increases from 1.98 nm to 4.98 nm, both of the peaks for *s*-polarized and *p*-polarized light blue-shift. As a result, the peaks in the total scattered light spectra (shown by green plot) also blue-shift.



FIGURE S4. Far-field radiation pattern of a modeled nanocluster at three different wavelengths. The incident light polarization is aligned with the x-axis. The patterns at 892.5 nm represent electric dipolar radiation and the patterns at 700 nm represent electric quadrupolar radiation, in both XY and XZ planes. At the wavelength of 808.7 nm, the quadrupolar mode shows up in the XY plane (shown by the black arrows).



FIGURE S5. Transmission electron micrograph (left) and extinction spectrum (right) for gold nanoshells with 200 nm silica cores and 25 nm gold shells made using the same seeded-growth particle used to coat the silica satellites on the nanoclusters.

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