Supporting Information

Highly Tunable Plasmonic Assemblies of Gold Nanoparticles: in-Plane Manipulating Plasmon Coupling with Nanometer Precision

Alexandra I. Zvyagina, Alexander A. Ezhov, Vladimir K. Ivanov, Vladimir V. Arslanov, Maria A. Kalinina*

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S1. Materials and methods

Materials. All chemicals used were of analytical reagent grade. Stearic acid and octadecylamine were obtained from Fluka. Chloroform (Merck) was used as a solvent for the preparation of SA and ODA solutions with the concentrations 1.18 mM and 1 mM, respectively. Gold hydrosol was synthesized by a common procedure for citrate reduction of HAuCl₄^[1] (Acros Organics, Belgium) in water deionized to 16 M Ω cm resistivity (see S1A for details). For asprepared nanoparticles, the surface plasmon band appears at 519–520 nm in the UV–vis adsorption spectra (Fig.S1). Average radius of 18±1 nm was routinely estimated from DLS data; the synthetic yield corresponds to a number of nanoparticles of ~10¹⁵ L⁻¹. The pH of gold hydrosol was 6.7±0.1. The synthesis of cerium oxide hydrosol was 6.5±0.1; DLS and TEM investigation gave an average size of 3 nm with a comparatively wide size distribution. To prepare mixed hydrosols with varied ratios of components, certain portions of gold and cerium oxide colloidal solutions were mixed directly and then appropriately diluted using 0.05 wt % sodium citrate solution.

Formation of HTPAs. The equimolar solution of SA and ODA in chloroform was obtained by mixing of solutions of individual components; the mixed solution was used immediately after

preparation. The interfacial films were formed by spreading SA/ODA mixture on the surface of colloidal solutions in glass vessels of known diameter at $20\pm1^{\circ}$ C. The amount of spread solution should correspond to the surface coating, in which the area per molecule of surfactant is close to that in a tightly packed Langmuir monolayer (ca. 20 Å²). ^[3] Spreading was done using an automatic micropipet (Gilson) delivering 1µL drops onto a subphase surface in a chessboard-like pattern to distribute the monolayer uniformly.

The as formed floating mixed SA/ODA films with adsorbed nanoparticles were deposited vertically with automatic dipper onto the various supports: (i) piranha-pretreated silicon wafers, (ii) quartz subsequently washed with chloroform and acetone, and (iii) mica with freshly formed surface by taping off the upper layers prior to the experiment. The transferring speed was 5 mm min⁻¹.

UV-Vis Spectroscopy. UV-vis extinction spectra of HTPAs were measured with fiber optic CCD spectrometer AvaSpec-2048 (Avantes) equipped with a 75 W DH-2000 deuterium-halogen light source (Ocean Optics). The light was incident with an angle of 90° to the film at the airwater interface and the reflected light from the surface was analyzed from 200 to 800 nm at 20 ± 1 °C. The UV-vis spectra were recorded with a time resolution down to 1 min after the monolayer was spread and solvent evaporated 15 min. The spectral response measured from the monolayer-covered subphase was normalized to that obtained from the monolayer-free subphase (gold hydrosol or hydrosols mixture), using AvaSoft supplied by the manufacturer and further transformed into extinction spectra. The spectra of HTPAs transferred onto quartz were measured using a two-beam spectrophotometer Shimadzu UV-2450. For comparison, the spectra were normalized to maximal extinction.

Scanning Electron Microscopy (SEM). Scanning electron microscopy images of LB films were obtained using a Carl Zeiss NVision 40 workstation at 1 and 5 kV accelerating voltages using secondary electron (SE2) detector. To distinguish between objects of different chemical composition, a back scattered electron (BSE) detector was also used. SE and BSE images were taken from the same spots to separate topographic and compositional contrast. The silicon-supported film surfaces were scanned at an electron beam accelerating voltage of 5 kV.

Atomic Force Microscopy (AFM). Atomic force microscopy images were obtained by the scanning probe microscope SOLVER P47-PRO (NT-MDT). Super sharp diamond-like carbon tips with typical curvature radius of 1 nm grown on the probe of the silicon cantilevers NSG01 DLC (NT-MDT) were used. Measurements were performed in semicontact mode with the amplitude of the probe oscillations from 1 to 5 nm (peak-to-peak).

Transmission Electron Microscopy (TEM). Transmission electron microscopy studies were carried out via a transmission electron microscope LEO912 AB OMEGA (Carl Zeiss). The accelerated voltage was 100 kV. Organic crystalline films with embedded nanoparticles were vertically transferred onto the copper grid coated with Formvar film.

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S2. Self-assembly of HTPA on a surface of citrate-stabilized gold hydrosol

Digital images of the experimental procedure. a) General view of the experimental setup; b) Experimental steps: 1 - quartz glass support in the dipper clip moves vertically downward into the hydrosol; 2 - fiber-optic sensor is placed over the interface and the spectral baseline is recorded; 3 - the mixture of SA/ODA surfactants in chloroform is spread over the hydrosol surface; 4 - the extinction spectra are recorded with a preset time intervals; 5 - when the desirable spectral pattern of interfacial assembly of surfactant-stabilized AuNPs is achieved, the support is slowly removed from the hydrosol to immobilize the as-prepared HTPA and then dried.

S2A. Synthesis of citrate-stabilized gold hydrosol

To synthesize a gold hydrosol, 7.25 mL of chloroauric acid (0.2 wt %) were added to 100 mL of deionized water under continuous stirring. The solution was heated to boiling, then 12.5 mL of sodium citrate (0.5 wt %) were added quickly, and the boiling mixture was stirred for 15 min. After the reaction completed, the colorless solution turned to wine-red. For the as-prepared colloidal gold, the stable LSP band appears at 519-520 nm in the UV-vis extinction spectrum. An average radius of gold nanoparticles was routinely estimated from DLS data; the synthetic yield corresponds to an average number of nanoparticles ~ $10^{15} L^{-1}$.



Fig. S2.1. The extinction spectrum of citrate-stabilize gold hydrosol.



Fig. S2.2. 2D spectral picture of self-assembly of gold HTPA recorded by fiber optic UV-vis extinction/reflection spectrometry; the extinction increases with time. The spectra were recorded starting from 25 min for 395 min with time resolution of 16 min, $T=20\pm0.5^{\circ}$ C.



Fig. S2.3. Solvent-induced aggregation of AuNPs on a surfactant-free surface of gold hydrosol. The citrate-stabilized nanoparticles do not normally aggregate spontaneously without any driving force applied because of electrostatic repulsion, at least, for a reasonable period of time. One can, nevertheless, initiate the non-controlled aggregation of particles on the surfactant-free surface by dissolving the citrate-stabilizing layers of the adsorbed particles using the excess of organic solvent. We performed this experiment by spreading and evaporating 2 ml of chloroform on a surface of gold hydrosol. The spectra of the surface were measured (*1*) before the spreading and (*2*) after the complete evaporation of the solvent. The comparison of the spectra of solvent-induced aggregates shows the red-shift of LSP band with the appearance of absorption at wavelengths >700 nm due to the formation of direct metal-metal interface between aggregated particles because of the loss of citrate stabilizing shell.





Fig. S2.4. Large-scale SEM images of typical HTPAs formed at different time intervals after spreading of organic mixture onto a surface of gold colloidal solution and transferred onto silicon wafer supports: (a) 90 min, (b) 110 min, (c, d) 180 min (for the same film at different magnification).

S2B. Interplay between the plasmon coupling and structural changes in HTPAs

As evidenced by SEM examination, the distance between the nearest adjacent AuNPs in HTPA does not change significantly during formation of the nanoparticle network. Both our experimental results and published data show that that the wavelength of the maximum of LPB in isotropic aggregates of AuNPs of similar size located near the 600-670 nm.^[4-7] This band is produced by the excitation of collective modes of plasmons and its spectral position primarily depends on the distance between adjacent AuNPs. Literature data suggest that, for AuNPs with a size ~20 nm, the position of this collective mode resonance peak in the vicinity of 700 nm corresponds to the formation of linear chains of AuNPs wherein the chains are separated far apart. ^[6-9] The distance between adjacent AuNPs in such chains must be less than 1 nm, thereby determining the wavelength of the maxima of longitudinal collective mode.^[10,11] It has been also shown that, for AuNPs ~18 nm in size assembled into linear straight chain, the change of the distance between adjacent AuNPs from 0.5 nm to 3 nm leads to the shift of the peak of longitudinally coupled plasmon mode from 690 nm to 570 nm.[10] Taken together, our experimental results and literature data suggest that the distance between adjacent AuNPs is approximately 1 nm (the distances significantly exceeding this value would be clearly resolved in SEM images), and the optical properties of HTPAs are determined by the morphology of the aggregates.



Fig. S2.5. Comparative data on UV-vis spectra of non-percolated structure of HTPA, formed on a surface of gold colloid at 45 min and then transferred onto quartz supports. Red and black lines correspond to the extinction spectra recorded before and after the transferring HTPA onto the quartz surface. Figure S2.5b shows that in some samples the far red-shifted shoulder also appears, most likely, because of the loss of a certain portion of the citrate coating during vertical

deposition of the assembly of AuNPs, which are not yet fully stabilized with the surfactant mixture.

S3. Self-assembly of binary HTPAs comprising CeO₂NPs and AuNPs

S3A. Synthesis of citrate-stabilize hydrosol CeO₂NPs

A citrate-stabilized ceria aqueous sol was synthesized by the previously reported procedure.^[12] Briefly, 0.24 g of citric acid was mixed with 25 mL of a 0.05 M aqueous cerium(III) nitrate solution. The resulting solution was rapidly poured under stirring into 100 mL of a 3 M ammonia solution, and then exposed for 24 h at ambient conditions. Then the solution was purified from precursors and by-products by sedimentation and further re-dispersion.



Fig. S3.1. UV-vis extinction spectrum of cerium oxide hydrosol, T=20±0.5° C



Fig. S3.2.TEM images of CeO₂NPs deposited onto Formvar-coated TEM grid from colloidal solution.



Fig. S3.3.TEM images of two different magnifications for the same film of SA/ODA with aggregated CeO₂NPs; the coating was formed through the adsorption of CeO₂NPs from citrate-stabilized hydrosol under conditions similar to those for fabricating gold HTPAs.



Fig. S3.4. Dynamic spectral picture of binary HTPA forming on the surface of mixed hydrosol with CeO₂NPs/AuNPs ratio of 0.5 and recorded by the fiber optic UV-vis extinction/reflection spectrometer. The spectra were recorded for 60 min with time resolution of 2 min, the extinction increases with time. T= $20\pm0.5^{\circ}$ C



Fig. S3.5. UV-vis spectra of floating HTPA on a surface of mixed hydrosol with CeO₂NPs/AuNPs ratio equal 100:1. The spectra were recorded for 60 min with time resolution of 10 min, $T=20\pm0.5^{\circ}$ C.









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Fig. S3.6 AFM image (A, B) and surface profiles (C-G) of the film with CeO₂NPs/AuNPs HTPA transferred onto mica supports. Directions of the cross sections (C-G) are shown in figure (B) with lines S1-S5.

S4. Self-assembly of binary HTPAs comprising SiO₂NPs and AuNPs

S4A. Binary HTPAs harboring silica and gold nanoparticles were fabricated via the same procedure as that used for mixed cerium oxide/gold HTPAs. Aqueous sol of non-stabilized silica nanoparticles (100-120 nm) was mixed with citrate-stabilized gold colloid and then diluted with 0.05 wt % sodium citrate solution to produce mixed colloid with an appropriate ratio of nanoparticles. The mixture of surfactants was spread on to a surface of two-component colloidal solution; the as-formed HTPAs were transferred onto silicon wafer and investigated by SEM.



Fig. S4.1. SEM images of HTPA, formed on a surface of mixed hydrosol with a AuNPs/SiO₂NPs ratio of 1:1 and immobilized on a silicon wafer.



Fig. S4.2. SEM images of HTPA formed on a surface of mixed hydrosol with a $AuNPs/SiO_2NPs$ ratio of 1:5 and immobilized on a silicon wafer. When the amount of silica nanoparticles is large, they aggregate at the interface through V-d-W interactions, which induce a collapse of 2D structure of AuNPs on the surface of aggregated SiO₂. The enhanced hydrophobic interactions between such semi "core-shell" silica particles increases aggregation even more and results in formation of 3D collapsed structure.

S5. References

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