Supporting Information:

Evolution of ligand-capped nanoparticle multilayers toward a near unique thickness

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Size of AuNPs from UV-vis and TEM

The size of thiol-coated Au-nanoparticles (AuNPs), as presented in ESI of Ref. 1, is reproduced here for easy reading. The optical absorption spectra of AuNPs in toluene solution were collected with a UV-vis spectrophotometer (Lambda 750, Perkin Elmer), while the transmission electron micrographs of the AuNPs, deposited on a carbon-coated copper grid, were observed using transmission electron microscope (JEM 2100, JEOL). Typical UV-vis spectrum and TEM image for the AuNPs are shown in Fig. S1. A broad hump near 520 nm is observed in the optical absorption spectrum (Fig. S1a), which is a characteristic surface plasmon resonance (SPR) band of the core AuNPs. The peak becomes quite prominent, after subtraction of exponentially decaying background. The size of the core AuNPs ($2R$) is estimated from the full width at half maximum (FWHM) of this peak, which is about 2.5 nm. Formation of AuNPs is also evident from TEM image (Fig. S1b) and corresponding particle size histogram is shown in the inset. The value of $2R$, as estimated from the particle size distribution curve, is 2.5±0.6 nm, which is consistent with the size estimated from optical absorption measurement. The average size of the overall AuNPs is then about 4.5 nm, as the dodecanethiol capping thickness is nominally assumed to be 1 nm.

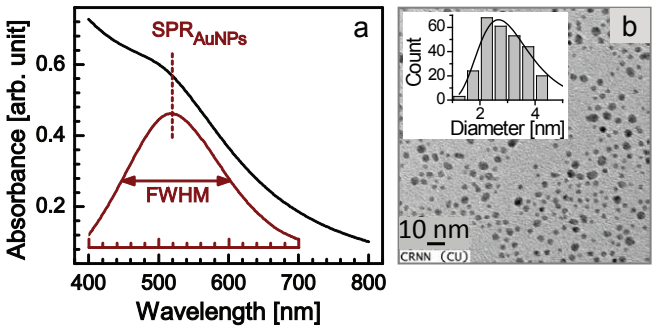

Fig. S1 (a) UV-vis spectrum of AuNPs in solution and corresponding background subtracted spectrum to emphasize the SPR peak and its FWHM and (b) typical TEM image of AuNPs in grid and corresponding size histogram in the inset.

$\Pi - A$ isotherm of AuNP Langmuir monolayer

The pressure-area ($\Pi - A$) isotherm of AuNP Langmuir monolayer was reported before (in Ref. 1). In short, a 1.5 ml toluene solution of AuNPs (0.5 mg ml^{-1}) was spread uniformly, using a micropipette, on the surface of Milli-Q water in a Langmuir trough (KSV 5000). It was kept undisturbed for some time to let the toluene evaporate and the hydrophobic AuNPs lay suspended at the air-water interface (at 23°C). Typical $\Pi - A$ isotherm of AuNP Langmuir monolayer on water surface, as reported before (in Ref. 1), is shown in Fig. S2. Gaseous (G), liquid-expanded (LE) and liquid-condensed (LC) phases, corresponding to the isotherm, are indicated in Fig. S2. Also the five different pressure, where LS films were deposited, are marked in Fig. S2. The approach speed, contact duration and removal speed used for the transfer process were 1 mm/min, 15 s and 1 mm/min, respectively. Multi-transfer was performed by slightly shifting the substrate horizontally each time, as the network-like structure of Langmuir monolayer restricts the fast in-plane diffusion of the AuNPs towards the transferred area. The samples were then preserved at the X-ray laboratory, where the temperature and relative humidity were maintained at ∼25°C and ∼40%, respectively.

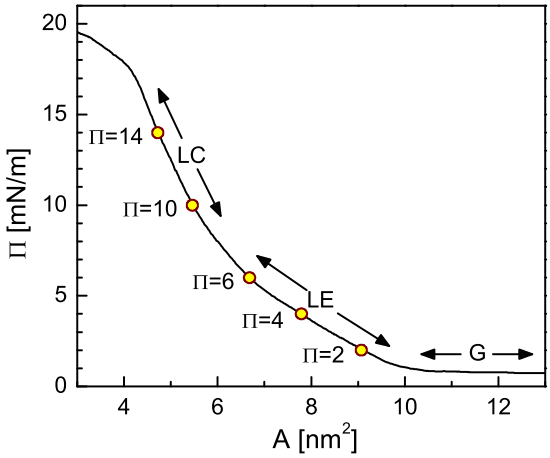

Fig. S2 Pressure-area ($\Pi - A$) isotherm of the AuNP layer, recorded in a Langmuir trough, showing various phases, namely gaseous (G), liquid-expanded (LE) and liquid-condensed (LC) as reported before (in Ref. 1).

EDP of an AuNP

The structure of an AuNP is shown schematically in Fig. S3. The EDP of such core-shell structure can be calculated by adding the contributions from the two different parts having different electron densities and can be approximated with a Gaussian peak function, as shown in Fig. S3 and can be presented as (Ref. 2)

$$\rho(z) = \rho_0 \exp[-(z/\sigma_0)^2]$$

where $\rho_0 \approx 1.8$ e Å^{-3} is the peak electron density and $\sigma_0 \approx 1.04$ nm is the standard deviation (or peak width related term).

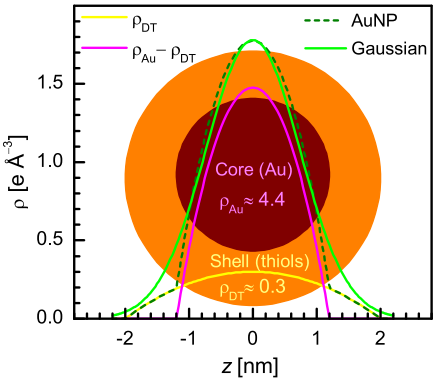

Fig. S3 Schematic of an AuNP, where the core is of high density Au ($\rho_{\mathrm{Au}} \approx 4.4$ e Å^{-3}) and the shell is of low density thiols ($\rho_{\mathrm{DT}} \approx 0.3$ e Å^{-3}). Corresponding variations of calculated electron density as a function of height (relative to the center of AuNP); for the complete NP of size ≈ 4 nm and $\rho \approx \rho_{\mathrm{DT}}$, for the core NP of size ≈ 2.5 nm and $\rho \approx \rho_{\mathrm{Au}} - \rho_{\mathrm{DT}}$ (≈ 4.1 e Å^{-3}), for the linear combination of them and for the equivalent Gaussian function (Ref. 2).

EDPs of monolayers of AuNPs

The typical monolayer structures along in-plane and out-of-plane directions are shown in Fig. S4. The EDP of such monolayer can also be expressed through a Gaussian peak function as

$$\rho(z) = \rho_f \exp[-(z/\sigma_f)^2]$$

where ρ_f is the peak electron density and σ_f is the standard deviation (or peak width related term) of the monolayer consisting of AuNPs in 2D-hexagonal structure. For perfect monolayer structure, where all AuNPs are at same z position, $\sigma_f \approx 1.04$ nm and $\rho_f \approx 1.8$ e Å^{-3}. On the other hand, $\sigma_f \approx 1.15$ nm represents near monolayer structure where z positions of AuNPs varies slightly and corresponding $\rho_f \approx 1.6$ e Å^{-3}. EDPs for both the conditions are shown in Fig. S4.

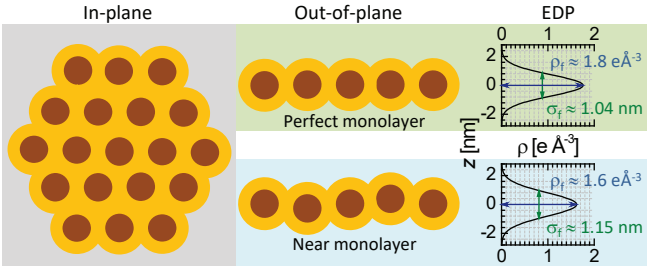

Fig. S4 Schematics of perfect monolayer and near monolayer of AuNPs, showing in-plane and out-of-plane structures and EDPs. The peak electron density (ρ_f) and the standard deviation (σ_f, which is related to the peak width) of the EDPs (represented by equivalent Gaussian functions) are indicated.

References

[1]M. Mukhopadhyay and S. Hazra, *RSC Adv.*, 2016, **6**, 12326–12336
[2]M. Mukhopadhyay and S. Hazra, *Phys. Chem. Chem. Phys.*, 2018, **20**, 1051–1062