Supplementary Information (SI) for Nanoscale.

3D Au Nanoparticle Lattices in MoO_3 for Tunable Optical and Thermo-Electrical Properties

1. SEM MEASUREMENTS

Scanning electron microscopy measurements are performed on the surface of the film Au4T3 with the largest Au NPs. The surface morphology is given in Fig. S1(a).

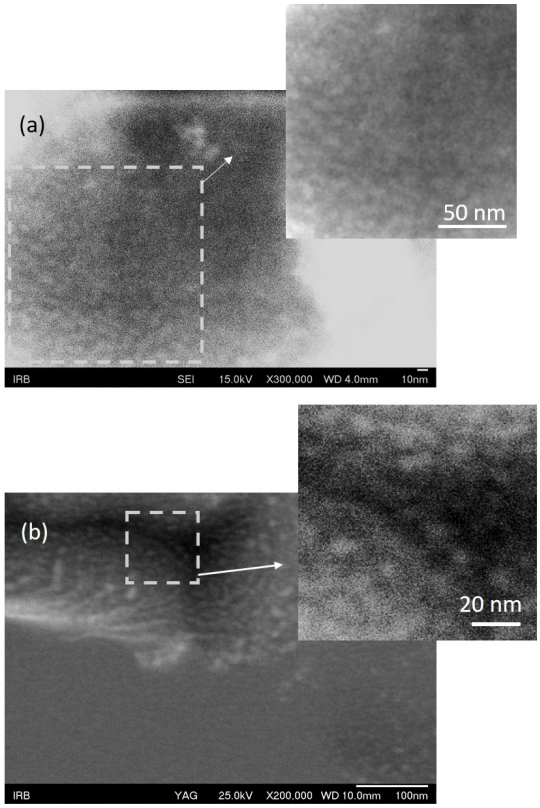

Fig. S1. SEM measurements of (a) surface and (b) NPs visible inside scratch on it, for the film Au4T3.

2. STATISTICAL DISTRIBUTIONS OF NP SIZES AND SEPARATIONS

Statistical distributions of the NP radii and ordering parameters are determined by numerical analysis of GISAXS maps (given in Table 2 of the manuscript). The distributions of the NP radii are given in Fig. S2(a)-(c). Using these values, the distributions of the NP separations to the nearest neighbors are calculated assuming BCT ordering of the Au NPs. The separations in the direction parallel to the film's substrate (along basis vectors $\vec{a_1}$ or $\vec{a_2}$) and in the direction along the basis vector $\vec{a_3}$, all shown in Fig. 1(d) of the manuscript (vertical separation) are shown in Figs. S2(d-f) and (g-i), respectively.

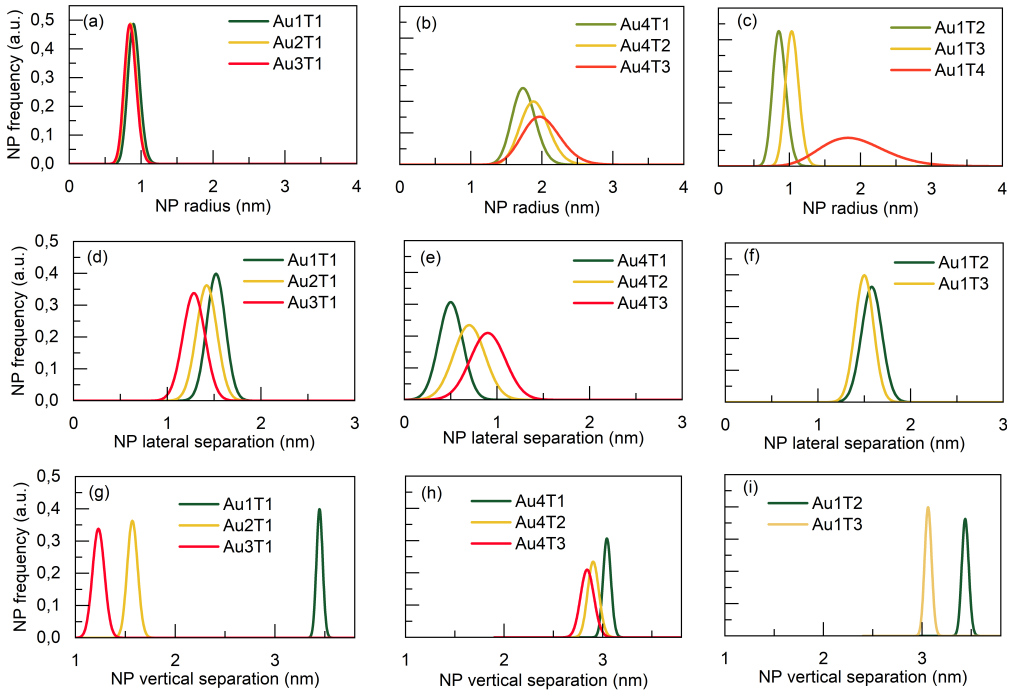

Fig. S2. Statistical distributions of Au NP: (a)-(c) radii, (d)-(f) lateral separations along basis vectors $\vec{a_1}$ or $\vec{a_2}$, and (g)-(i) separations along basis vector $\vec{a_3}$ (vertical separations) obtained assuming BCT arrangement of NPs, for three series of the investigated films.

3. THEORETICAL MODEL

The obtained dependence of the LSPR peak position on the wavelength (Figure 6 of the manuscript) can be modeled by the optical extinction spectra using the Mie theory taking into account only the dipole absorption term[1, 2]:

$$C_{ext} \propto \frac{r^3 \varepsilon_m^{3/2}}{\lambda} \frac{\varepsilon_i}{(\varepsilon_r + 2\varepsilon_m)^2 + \varepsilon_i^2}, \tag{S1}$$

where ε_m is the refractive index of the medium and λ is the wavelength for frequency ω. However, this model is not sole Mie theory, but can rather be interpreted as quantum corrected model where a correction is introduced via the size dependent complex dielectric function $\varepsilon = \varepsilon_r + i\varepsilon_i$ and size dependent C parameter, as explained in what follows.

We modify the Mie theory by decomposing the real (ε_r) and imaginary (ε_i) part of the noble metal dielectric function into two terms, a free electron term and an interband, or bound electron, term[1]. Since the dielectric function is additive, it can be written as

$$\varepsilon_{bulk}(\omega) = \varepsilon_{bound}(\omega) + \varepsilon_{free}(\omega) \tag{S2}$$

For bound electrons, the complex dielectric function can be calculated taking into account the interband transitions from the d-band to the conduction sp-band near the L point in the Brillouin zone of gold[3]. Inouye et al.[4] have shown a simplified expression of this calculation assuming that the curvature of the d-band can be ignored:

$$\begin{aligned} \varepsilon_{bound}(\omega) = Q_{bulk} \int_{\omega_g}^{\infty} \frac{\sqrt{x - \omega_g}}{x} [1 - F(x,T)] \\ \times \frac{(x^2 - \omega^2 + \gamma_b^2 + i2\omega\gamma_b)}{(x^2 - \omega^2 + \gamma_b^2)^2 + 4\omega^2\gamma_b^2} \mathrm{d}x, \end{aligned} \tag{S3}$$

where $\hbar\omega_g$ is the gap energy (E_g) for gold; $F(x, E_F, T)$ is the Fermi energy distribution function of

conduction electron of energy $\hbar x$ at the temperature T with Fermi energy E_F; γ_b represents the damping constant in the band to band transition and Q_{bulk} is a proportionally factor.

The complex dielectric function for the free electrons can be written as usual:

$$\varepsilon_{free}(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma_{free}\omega}, \tag{S4}$$

where ω_p is the bulk plasma frequency and γ_{free} is the electron damping constant in the Drude model.

The excellent agreement of this theory with the experimental data was nicely presented by Scaffardi et al.[5] who choose the parameters in equations (S3) and (S4), such as Q_{bulk}, E_g, E_F, ω_p and γ_{free} to fit the experimental dielectric function values for bulk gold taken from Johnson and Christy[6].

Here, too, we assume the plasma frequency ω_p to be independent of size. However, the damping, which depends on the mean free path of the free electrons, is significantly influenced by the size of the particles. For particles that are smaller than the mean free path of the conduction electrons in the bulk material, collisions with the particle boundary dominate the mean free path[7–9] and therefore increase the damping constant associated with the contribution of the free electrons

$$\gamma_{free}(R) = \gamma_{bulk} + C\frac{v_F}{R}, \tag{S5}$$

where v_F is the electron velocity at the Fermi surface and R is the radius of the particle. Parameter C is particularly interesting, and yet not fully understood. It is the scattering constant that includes details of the scattering processes. Its actual value is not free from controversy. In our calculations, we fit the experimental data by letting C to also vary with R.

REFERENCES

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