Electronic Supplementary Information

Gold Nanoparticle Superlattices: Structure and Cavities Studied by GISAXS and PALS

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XPS measurements

The synthesis of 1-dodecanethiol (DDT)-stabilized GNPs is based on the reduction of chloro(triphenylphosphine)gold(I) with *tert*-butylamine borane complex in the presence of DDT. The as-synthesized particles were purified by precipitation with ethanol. For reliable PALS measurements a quantitative elimination of nitrogen compounds is required, as these have been shown to quench positronium[1,2]. As confirmed by XPS measurements and elementary analysis (detection limit of 0.5 %) the samples prepared and purified as described in the experimental section did not reveal any contamination with nitrogen compounds (see XPS spectra below, Figure S1).

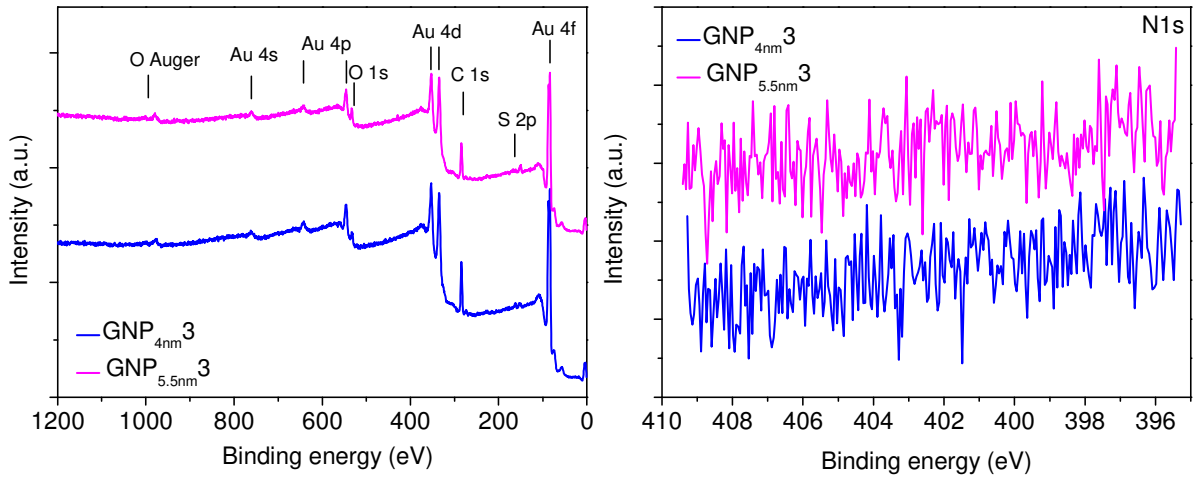

Figure S1: XPS spectra (left: survey, right: N region) of GNP superlattice films prepared from sample $GNP_{4\ nm}3$ (blue) and $GNP_{5.5\ nm}3$ (magenta). In the survey spectra the expected signals for the elements Au, C and S and some O (due to the exposure to atmosphere prior to the XPS measurements) are observed. The absence of a peak in the energy range between 395 to 410 eV reveals that no nitrogen compounds were detectable.

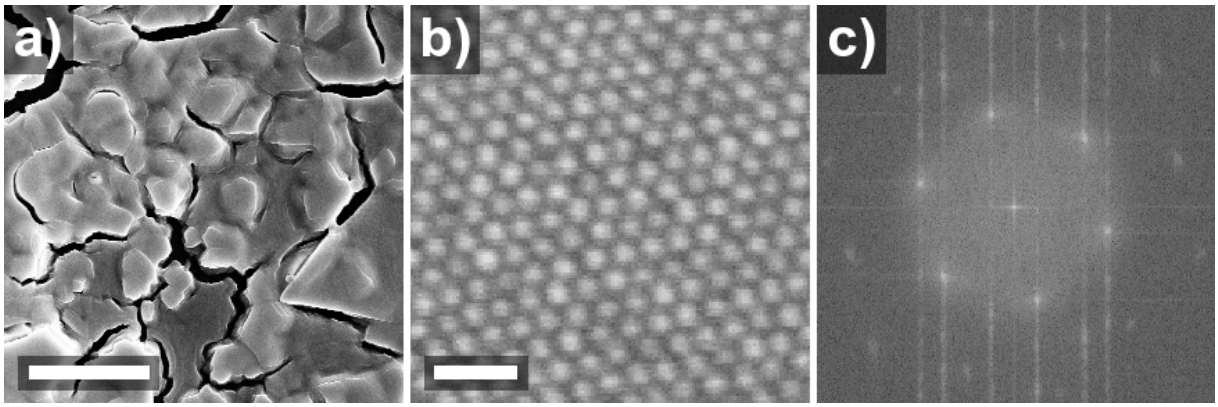

Figure S2: a), b) SEM images of samples $GNP_{5.5\ nm}1$ shown at two different magnifications and c) the Fourier transform of the SEM image presented in Figure part b). The scale bars are 10 µm in a) and 20 nm in b).

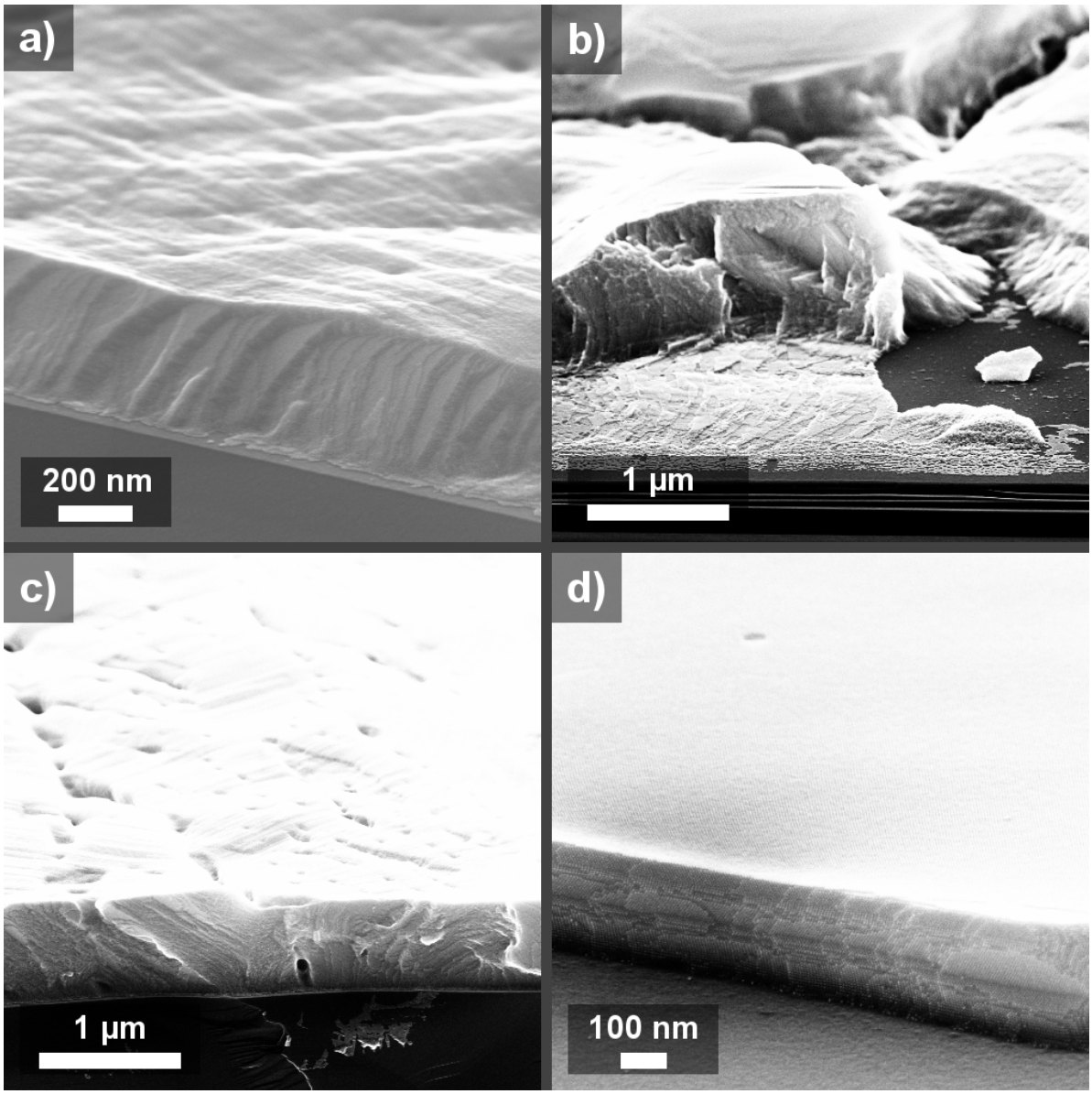

Figure S3: Representative SEM images of samples a) $GNP_{4\ nm}1$, b) $GNP_{5.5\ nm}1$, c) $GNP_{4\ nm}2$, and d) $GNP_{5.5\ nm}2$ providing cross-sectional views of the cleaved samples.

Calculation of gold content

$$n_{\mathrm{Au}} = \frac{m_{\mathrm{Au}}}{m_{\mathrm{Au}} + m_{\mathrm{DDT}}}$$

$$m_{\mathrm{Au}} = f_{\mathrm{Au}} \cdot \rho_{\mathrm{Au}}$$

$$f_{\mathrm{Au}} = \frac{r^3}{r_{\mathrm{eff}}{}^3} \cdot 0.74$$

$$r_{\mathrm{eff}} = r + \frac{\delta}{2}$$

$$m_{\mathrm{DDT}} = f_{\mathrm{DDT}} \cdot \rho_{\mathrm{DDT}}$$

$$f_{\mathrm{DDT}} = 1 - f_{\mathrm{Au}}$$

with

n_{Au}: mass/mass fraction of gold

m_{Au}: mass/volume fraction of gold

m_{DDT}: mass/volume fraction of DDT

f_{Au} respectively f_{DDT}: volume/volume fraction of gold respectively DDT

ρ_{DDT}: density of DDT (0.845 g/cm³)

ρ_{Au}: density of gold (19.32 g/cm³)

r: radius of the gold cores (from TEM measurements)

δ: interparticle edge-to-edge distance obtained by subtracting the TEM-diameter of the gold cores from the center-to-center nearest neighbor distance determined by GISAXS

References

1 O. E. Mogensen, in *Springer Series in Chemical Physics*, ed. V. I. Goldanskii, Springer-Verlag, Berlin, Heidelberg, 1995, vol. 58.

2 Y. C. Jean, P. E. Mallon and D. M. Schrader, *Principles and Applications of Positron and Positronium Chemistry*, World Scientific, New Jersey London Singapore Hong Kong, 2003.