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#### Supporting Information (SI) for

Comment [MC]:

#### Precise size control of hydrophobic gold nanoparticles in the 2-5 nm range

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#### Materials

All chemicals were used as received without further purification.

Hydrogen tetrachloroaurate(III) hydrate (HAuCl<sub>4</sub>.xH<sub>2</sub>O 99.8%) and chlorotriphenylphosphinegold(I) (AuCl(PPh<sub>3</sub>) 98%) were purchased from Strem Chemicals. Hexadecanethiol 95%, tetraoctylammonium bromide 98%, borane tert-butylamine complex 97% and sodium borohydride 96% were purchased from Merck. Toluene 99% and ethanol 96% were purchased from Fisher Scientific.

#### SAXS

Small Angle X-ray Scattering (SAXS) measurements were performed using the home-made MODIX instrument (LPS, Orsay). A rotating anode X-ray generator (40 kV, 40 mA) is equipped with a molybdenum target (wavelength Mo K $\alpha$ =0.71 Å, energy 17 keV) and a collimating multilayer X-ray optic (Max-Flux optic, RIGAKU). Samples were prepared in glass capillaries (diameter 2 mm) filled with a 1 wt% solution of nanoparticles in toluene and placed on the motorized sample holder of the instrument. 2D SAXS images were acquired on a two-dimensional image-plate detector (MAR 345 mm). Data reduction to the radially averaged intensity I(q) was done using the NIKA macros written for IgorPro (Wavemetrics, Oswego, USA).<sup>1</sup> The sample to detector distance of 760 mm was calibrated using a quartz powder. The range of scattering vectors q was between 0.05 Å<sup>-1</sup> and 3.1 Å<sup>-1</sup>.

The SAXS intensity curves I(q) were fitted with the SasView software (<u>https://www.sasview.org/</u>) using a polydisperse sphere model with a Schultz-Zimm distribution. To be consistent with the TEM data, the mean diameter  $D_{SAXS} = 2 R_{SAXS}$  is derived from the fit results. The fit parameters are  $R_{SAXS}$ , the nanoparticles mean radius, and  $p_{SAXS}$ , the polydispersity ratio given by  $p_{SAXS} = \sigma_{SAXS}/D_{SAXS}$  where  $\sigma_{SAXS}$  is the standard deviation of the mean diameter.

## TEM

Samples were observed with a JEOL 2010 Field Emission Gun (FEG) transmission electron microscope operated at 200 kV and imaged at 400k magnification. Images were collected on a Gatan Ultrascan 4K CCD camera.

The TEM images of the monolayer films were obtained by using a JEOL JEM2100 equipped with a LaB<sub>6</sub> thermionic electron gun and a High Tilt objective pole piece. The microscope was operated at 200 kV with a point-to-point resolution of 0.25 nm.

Manual measurements of the particles size were done with ImageJ software on 100 nanoparticles. Their mean diameter  $D_{TEM}$  and its standard deviation  $\sigma_{TEM}$  were calculated. The polydispersity ratio  $p_{TEM}$  is defined by:  $p_{TEM} = \sigma_{TEM} / D_{TEM}$ .

### HRTEM

High-resolution STEM images were obtained using a JEM-ARM200F Cold FEG NeoARM operating at 200kV.

### **UV-visible spectroscopy**

The UV-visible spectra were recorded with a Cary 5000 spectrometer, using toluene suspensions of nanoparticles in glass cuvettes. The spectra were scaled at an absorbance of 0.5 at 400 nm in order to compare them with a similar gold concentration.

## **Particles synthesis**



**Scheme S1.** Illustration of the different steps to follow for the synthesis of AuNPs of desired diameter  $D_{f}$ .

#### Step 1: seeds synthesis

The 2 nm seeds were synthesized as follow: 393 mg of  $HAuCl_4.xH_2O$  were dissolved in 20 mL of water. The gold ions were then extracted with a solution of 1.37 g of TOAB in 80 mL of toluene and the colorless aqueous phase was discarded. The organic phase was transferred in a three-necked round bottomed flask and 616  $\mu$ L of hexadecanethiol were added. The

mixture was heated at 60°C and NaBH<sub>4</sub> (358 mg in 15 mL of water) was added dropwise in 15 minutes. After 30 minutes at 60°C, the reaction medium was allowed to stir for 3 hours at room temperature. The aqueous phase was removed, the particles were concentrated with a rotary evaporator (45°C, 80 mbar), precipitated with ethanol, centrifuged, washed a second time and redispersed in 10 mL of toluene to give a mother solution with a gold concentration [Au(0)].

### Step 2: characterization of the seeds size and concentration

- The size of the seeds was determined by SAXS (see appropriate section).

- The UV-visible spectrum of the seeds was recorded with a precise dilution from the mother solution (20  $\mu$ L of mother solution + 2 mL of toluene). According to Scarabelli *et al.*<sup>2</sup>, the gold concentration was calculated thanks to the absorbance at 400 nm (an absorbance of 1.2 corresponds to a concentration of [Au(0)] = 0.5 mM for a path length of 10 mm). The relative error on this concentration is 1.5%, coming from the dilution procedure and the absorbance measurement itself. Here, the absorbance at 400 nm was 2.39, so the concentration of the mother solution was [Au(0)] = 100.6 mM. Then, 15 identical batches of 497  $\mu$ L of particles were prepared and let to dry, so every dried batch contained 5.10<sup>-5</sup> mol of Au(0). Making identical batches is necessary for the next steps.

### Step 3: seeds growth

The calculation of the gold precursor quantity that should be added  $(n_{add})$  to reach a given size was performed as follows:

$$n_{add} = (n_i^* D_f^3 / D_i^3) - n_i$$

With:

D<sub>i</sub>, the seeds diameter that was measured with SAXS (2.15 nm).

D<sub>f</sub>, the desired final diameter of the particles.

 $n_i$ , the initial quantity of gold, known to be 5.10<sup>-5</sup> mol.

## Example of protocol to reach 4 nm nanoparticles:

A batch of seeds  $(n_i)$  was redispersed in 4 mL of toluene and transferred into a round bottomed flask. 154 µL of hexadecanethiol  $(10*n_i)$  were added, followed by 46.5 mg of TBAB  $(2*n_{add})$ . The mixture was heated at 100°C in an oil bath and AuCl(PPh<sub>3</sub>) (132.4 mg in 22.6 mL of toluene,  $n_{add}$ ) was added with a syringe pump at a rate of 45 mL/h (10.8  $n_i$ /h). At the end of the addition, the heating was continued for 2 minutes and the particles were cooled back to room temperature, precipitated with ethanol and centrifuged.

## Step 4: adjustments (if needed)

This step must be done after the growth of the first seeds batch only if the obtained diameter  $D_f$  is not exactly the expected one.

The main error source on the calculation of  $n_i$  comes from the determination of [Au(0)] in the mother solution by absorbance measurement. To take this error into account, the strategy is to calculate the effective quantity of gold,  $n_{eff}$ , contained in each batch of seeds, considering that all the batches contain exactly the same gold quantity.

n<sub>eff</sub> is calculated as follows:

$$n_{eff} = n_{add} * D_i^3 / (D_{eff}^3 - D_i^3)$$

With:

D<sub>i</sub>, the seeds diameter measured with SAXS.

 $D_{eff}$ , the effective final diameter of the particles obtained from the first growth experiment.  $n_{add}$ , the quantity of precursor added to the seeds in this same experiment.

Then we consider that each batch of seeds contains the gold quantity  $n_{eff}$  instead of  $n_i$ .  $n_{eff}$  is used in the next batches to calculate the precursor quantity  $n_{add}$  that should be added to reach a given size.

# Self-assembly

Self-assembly experiments were carried out using a drying-mediated method.<sup>3</sup> A Teflon well with a cylindrical hole (diameter and height of 1 cm) filled with 0.5 mL of DEG was used as support. 20  $\mu$ L of Au NPs dispersion, prepared by dissolving the as-synthesized NPs in toluene (with a concentration of 2 mg/mL), were pipetted on the DEG surface in a Teflon well, which was then covered with a glass slide to slow the evaporation process. Toluene was let evaporate and a solid film formed after complete evaporation of the solvent. The membrane was recovered by placing a TEM grid using tweezers under the floating film and then gently lifted upwards to collect it. The substrates were then dried in a desiccator to remove residual DEG.

# Amount of lacunar defects

The amount of lacunar defects was calculated from the TEM image in Figure 3C using ImageJ. We counted the number of NPs in a 0.5  $\mu$ m<sup>2</sup> hexagonal monolayer (12718 NPs) and we calculated the number of NPs to cover the same area without any lacunas (12855 NPs). The number of missing NPs was estimated to be 137, which corresponds to 1 % of defect sites.



**Figure S1. A)** TEM picture of the seeds. Scale bar: 10 nm. **B)** X-Ray scattering curve of the seeds along with its fitting curve.



**Figure S2.** TEM pictures of every particles batches prepared from the seeds. For Au-5.50, the particles tend to merge together (inset). Scale bar: 10 nm.



Sample	D <sub>SAXS</sub> (nm)	Plasmon band position (nm)	
Seeds	2.16	/	
Au-2.50	2.44	/	
Au-2.75	2.73	492	
Au-3.00	3.00	500	
Au-3.25	3.27	504	
Au-3.50	3.52	508	
Au-3.75	3.74	510	
Au-4.00	4.04	512	
Au-4.25	4.26	514	
Au-4.50	4.55	515	
Au-4.75	4.78	516	
Au-5.00	5.08	518	
Au-5.50	5.54	518	

Figure S3. Evolution of the plasmon band position with the diameter of the particles.



Figure S4. X-Ray scattering curves of every particles batches.



**Figure S5.** Evolution of the standard deviation against the mean diameter of the particles in the present work and in the references  $^{4-7}$ .



**Figure S6.** TEM images of self-assembled Au NPs from samples Au-3.00, Au-4.00 and Au-5.00 and their FT. We can observe the improvement of the long-range hexagonal order by increasing the size of the NPs.

Sample	D <sub>calc</sub> (nm)	D <sub>saxs</sub> (nm)	P <sub>SAXS</sub>	X²
Seeds	/	2.147	0.092473	3.74480
Au-2.50	2.50	2.445	0.116260	0.35591
Au-2.75	2.75	2.729	0.104950	0.21564
Au-3.00	3.00	3.004	0.102550	0.33808
Au-3.25	3.25	3.271	0.097932	0.31030
Au-3.50	3.50	3.518	0.105280	0.52525
Au-3.75	3.75	3.792	0.092851	0.53017
Au-4.00	4.00	4.041	0.090633	0.97013
Au-4.25	4.25	4.261	0.093039	0.57725
Au-4.50	4.50	4.552	0.078784	0.84843
Au-4.75	4.75	4.776	0.084826	1.17360
Au-5.00	5.00	5.085	0.073195	0.58614
Au-5.50	5.50	5.548	0.073427	0.84055

**Table S1.** Data obtained from the fitting process with SasView software.  $D_{SAXS}$  is the mean diameter of the particles. The polydispersity ratio  $p_{SAXS}$  is defined as  $\sigma_{SAXS}/D_{SAXS}$  where  $\sigma_{SAXS}$  is the standard deviation of the mean diameter  $D_{SAXS}$ .  $\chi^2$  is the traditional reduced statistical parameter that reflects the quality of the fit.

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