

Supporting Information

Quantifying the Reflective Index of Nanometer-Thick Thiolated Molecular Layers on Nanoparticles

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Materials. All materials were used as received without any further purification. Chloroauric chloride ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$) and ascorbic acid were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Sodium borohydride (NaBH_4 , 98%), cetyltrimethylammonium chloride (CTAC, 98%) and 4,4'-biphenyldithiol (BPDT, 98%) was obtained from J&K Chemical Ltd (Shanghai, China). 1,4-Benzenedithiol (BDT, 98%) was received from TCI (Tokyo, Japan). p-Terphenyl-4,4''-dithiol (TPDT, 96%) was purchased from Aladdin (China). Nanopure

water ($>18.0\text{ M}\Omega\text{-cm}$) was used for all experiments. Note that the purity of CTAC is critical for the experiment and a high-enough purity ($\geq 98\%$) is recommended.

Characterizations. TEM images were collected from a JEM-2100F Transmission Electron Microscopy (JEOL, Japan) operated at 200 kV. UV-vis spectra were collected on a UV1900 UV-vis spectrophotometer (Aucybest, China) with a wavelength step of 0.1 nm and experimental accuracy of $\pm 0.3\text{ nm}$.

Synthesis of Au cores. Au cores were synthesized via a seed-mediated process. Typically, seed solution was firstly prepared by vigorous mixing of 10 mL of aqueous CTAC solution (0.1 M) and 515 μL of HAuCl_4 (4.86 mM) with 450 μL of NaBH_4 solution. The seed solution was aged for at least 1 h and then diluted for 10 times. Next, 10 mL of CTAC solution (0.1 M) was mixed with 515 μL of HAuCl_4 (4.86 mM) and 75 μL of ascorbic acid (0.04 M). Finally 20 μL of diluted seed solution was added into the solution under ultra-sonication and kept undisturbed in darkness for several days to obtain highly uniform spherical nanoparticles. The diameters of Au cores were measured in TEM images as $18.3 \pm 2.1\text{ nm}$.

Synthesis of molecule-decorated Au cores. The obtained CTAC-capped Au cores (1 mL) were washed for one time and then re-dispersed in water. The concentration of CTAC in Au core solution was reduced in favor of the adsorption of molecules on the Au cores, but it is still high enough to stabilize the Au cores. Then 50 μL of molecule solution (1 mM) was slowly added under vigorous ultra-sonication, and the mixture solution was kept for different time.

Synthesis of Au core-shell nanomatryoshkas (NMs). The molecule-modified cores were washed for three times by centrifuge at 10000 rpm for 15 min to remove excess reagents, and further dispersed in 0.5 mL aqueous CTAC solution (0.1 M). The Au

core-shell nanoparticles was prepared by adding 190 μL of molecule-modified core solution into the mixture of 4 mL CTAC solution (0.1 M), 200 μL of ascorbic acid (0.04 M), and 200 μL of HAuCl_4 (4.86 mM) under vigorous ultra-sonication. Finally, the obtained Au core-shell NMs were washed for three times and stored in aqueous CTAC solution.

Calculating the effective refractive index of molecular layers. The LSPR properties of Au nanoparticles are simulated through the finite difference time domain (FDTD) method using the program of FDTD Solutions (Lumerical Inc.). The smallest mesh size and the wavelength step of in the simulations are 0.01 nm and 0.1 nm, respectively. The NP decorated with a molecular layer was modeled as an Au sphere enclosed in a continuous and smooth molecular film. The dielectric data of Au come from Johnson and Christy [1] and are fitted by multi-coefficient model (MCM) from Lumerical in the simulations.

We also noticed that the initial Au cores in experimental section were coated by a bilayer of CTAC. According to our experiments, the zeta potentials of the initial Au core (+47.6 mV) and BDT-modified Au core (+48.3 mV) were almost the same. Considering the BDT layer is hydrophobic and electric neutral, it is reasonable to conclude the CTAC layer still stay around the Au core after BDT modification. For simplification we used the radius of CTAC micelles, 2.1 nm, as the length of CTAC layer [2]. The diameter of Au core was 18 nm, and the refractive index of CTAC was set as 1.378 [3]. Then we established the simulation models: Au core wrapped with CTAC layers (core-CTAC), and BDT-modified core wrapped with CTAC (core-BDT-CTAC). Then the CTAC-wrapped particle was assumed in water and the background refractive index is set to be 1.33.

The fitting method of the thickness histogram of ultra-thin molecular layers. The statistical thickness distribution histograms of the molecular layers were acquired by

the Gaussian fitting using the Origin software. Considering molecular multi-layer absorption, two-peak fitting with quasi limitations has been applied. The peaks are limited to the two local maximums with a freedom of ± 0.1 nm. The statistical thickness is finally gained when the fitting convergence is reached.

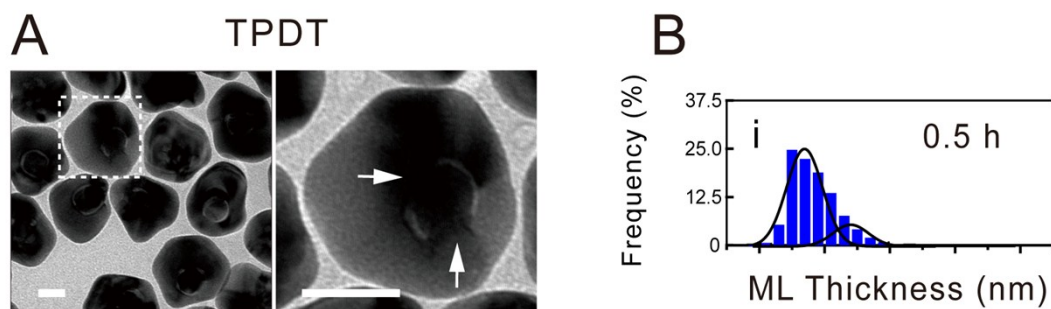


Fig S1. (A) TEM images of Au NMs embedded with TPDT molecular layers and (B) corresponding molecular layer thickness distribution histograms. The NMs are synthesized with 0.5 h incubation. All the scale bars are 20 nm. The white arrows in HRTEM image indicate the connections between core and shell.

We note that the incomplete nanogaps in NMs, for example 0.5 h TPDT-NMs, might bring in errors for the statistics since only the gap areas were measured. The metal bridges did exist but were bypassed in the histogram, which led to a slight over-estimation of the gap size. As shown in distribution histogram in Fig S1, the dominant thickness peak was centered at 0.85 nm for 0.5 h TPDT-NMs.

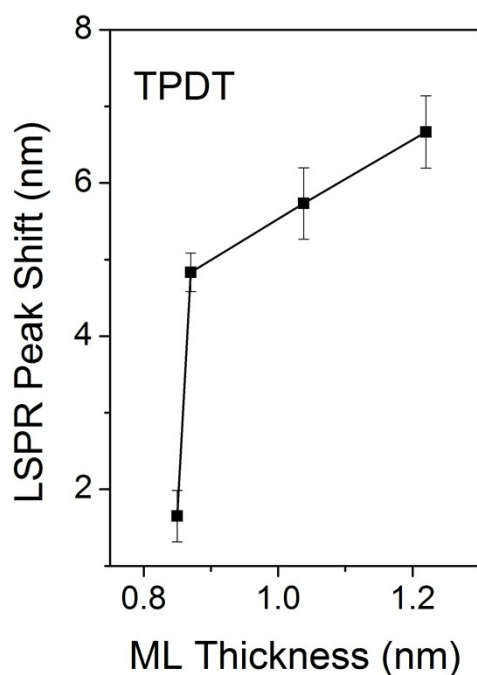


Fig S2. Measured LSPR shifts of Au cores decorated with TPDT.

If we put all four data together (Figure S2), we could see that the first data point at 0.5 h is not in line with the other three points (3, 5, 8 h). It is surprised to see that TPDT-decorated cores only exhibit a 1.7 nm red-shift for 0.5 h incubation time. This may be attributed to its insufficient molecular coverage. Considering the incompleteness of nanogaps may induce an error, we did not use the data of 0.5 h TPDT-NMs.

Table S1. The thickness of molecular layers, measured and calculated LSPR peak shift of three molecules modified Au core, and the corresponding N_{eff} values of the molecules.

	BDT			BPDT			TPDT		
Incubation Time (h)	0.5	3	8	0.5	3	8	3	5	8
Thickness (d, nm)	0.71	0.93	1.23	0.83	0.89	1.18	0.87	1.04	1.22
Measured LSPR shift (S, nm)	3.0	4.2	5.5	4.2	5.1	6.2	4.8	5.7	6.7
Calculated LSPR shift (S', nm)	3.1	4.1	5.7	4.5	4.8	6.3	4.8	5.7	6.6

R	3.2%	2.4%	3.5%	6.7%	6%	1.6%	0.0%	0.0%	1.4%
R_{Nor}	0.002867			0.0086			0.0002		
N_{eff}	1.59			1.65			1.66		

References

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