

Supporting Information

for Adv. Funct. Mater., DOI: 10.1002/adfm.202200148

Silica-Coated Gold Nanorod Supraparticles: A Tunable Platform for Surface Enhanced Raman Spectroscopy

Jessi E.S.van der Hoeven,* Harith Gurunarayanan, Maarten Bransen, D.A. Matthijsde Winter, Petra E.de Jongh, and Alfonsvan Blaaderen*

Supporting information:

Silica Coated Gold Nanorod Supraparticles: a Tunable Platform for Surface Enhanced Raman Spectroscopy

Jessi E.S. van der Hoeven^{a,b,§,*}, Harith Gurunarayanan^{a,§}, Maarten Bransen^a, D.A. Matthijs de Winter^a, Petra E. de Jongh^b, Alfons van Blaaderen^{a*}

^a Soft Condensed Matter, Debye Institute for Nanomaterials, Utrecht University, Utrecht, The Netherlands

^b Materials Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University, Utrecht, The Netherlands

[§] these authors contributed equally

*E-mail: j.e.s.vanderhoeven@uu.nl, a.vanblaaderen@uu.nl

Estimation of the Van der Waals attraction between Au@SiO2 NRs

The thin coated AuNRs were more prone to aggregation during the assembly, leading to the formation of some non-spherical, unordered supraparticles. The tendency of the thin coated AuNRs to aggregate can be ascribed to partial dissolution of the silica shell during the assembly process in the water droplets and/or Van der Waals attractions between the NRs. Such Van der Waals attractions were also found to be important in the self-assembly of much smaller (11 nm, FeO/CoFe₂O₄) NPs into supraparticles.¹

Strong attractions between colloidal particles can prevent the self-assembly into ordered structures. To assess if attractions played a role in our assembly experiments we estimated the Van der Waals interaction between two nanorods. Herein, the Au NRs were approximated as cylinders with radius R = 8.7 nm and length L = 95.7 nm. The attraction due to Van der Waals forces between two parallel NRs was estimated by using the following formula:^{2,3}

$$U_{vdW}(z) = -\frac{3}{8\pi} A_H \frac{(\pi R^2)^2 L}{z^5}$$

where z is the separation between the two cylinder axis and A_H is the Hamaker constant, for which values between 20 and 73 k_BT have been reported for gold in water.² We used the latter value to estimate the upper bound of this interaction when the two NRs are in contact, that is U_{vdW} (z = 2R+2h) = $-7k_BT$, where h = 3 nm is the silica shell thickness. The Van der Waals attractive interactions can be balanced by the electrostatic repulsion between the silica shells. The electrostatic repulsion depends on the conductivity of the solvent and the charge of the silica shells. This means that the effective interaction can be tuned via the thickness and charge of the silica shells around the Au-cores. Although -7 k_BT is significant, it is possible that in our experiments the Van der Waals forces between the gold cores were completely screened and attractions did not play a crucial role in the self-assembly. This is supported by the lack of clear evidence for a strong preference for side-to-side arrangement (that is extremely favorable for attractive rods) in the electron microscopy images.

References

University Press, 2006.

¹ F. Montanarella, J. J. Geuchies, T. Dasgupta, P. T. Prins, C. van Overbeek, R. Dattani, P. Baesjou, M. Dijkstra, A. V. Petukhov, A. van Blaaderen, and D. Vanmaekelbergh, Nano Letters, 2018, **18**, 3675–3681
² V. Parsegian. *Van der Waals forces: a handbook for biologists, chemists, engineers, and physicists*. Cambridge

³ Y. Nagaoka, T.Wang, J. Lynch, D. LaMontagne, and Y. Cao, Small, 2012, 8, 843-846

Supporting Figures



Figure S1 - Tuning of the silica shell thickness via the reaction time and temperature. 3 nm (a, red), 5 nm (b, orange) and 7 nm (c, blue) thick silica shells were obtained when coating the AuNRs for 15 min, 1 h, and 4 hours at 60 °C, respectively. d) The silica shell thickness plotted as a function of the reaction time at fixed reaction temperature of 60 °C. e) Plot of the silica shell thickness as a function of the reaction temperature with a fixed reaction time of 2 h.



Figure S2 – Oxidative etching of mesoporous silica coated AuNRs. a) VIS-NIR extinction spectra of the Au@SiO₂ NR in methanol during etching with 50 mM H_2O_2 and 0.24 M HCl at 60 °C. b) LSPR peak position shift of Au@SiO₂ NR at different time intervals during etching with 50 mM H_2O_2 and 0.24 M HCl at 60 °C in methanol. c) Photograph image of samples collected at time intervals 0, 15, 30, 45, 60, 75, 90, 95 and 97 min during oxidative etching. d) TEM image of Au@SiO₂ NR before etching and e) after etching.



Figure S3 - Probing the accessibility of silica coated AuNRs with different shell thickness and porosity. a) Raman spectra of pyridine (10 mM in H₂O) recorded in the presence of Au@SiO₂ NRs with a non-mesoporous shell thickness (d_{shell}) of 2 (blue), 5 (orange) and 7 nm (red). b) Raman spectra of pyridine recorded in the presence of Au@SiO₂ NRs with non-mesoporous and mesoporous shells with a pore size (d_{pore}) of <1 (red), 2.5 (orange) and 4-5 nm (blue) and d_{shell}= 16, 18 and 35 nm, respectively. The Au@SiO₂ NRs were dried on a silicon wafer before exposing them to the pyridine solution. Each spectrum in the plot is an average of 5 Raman spectra recorded on different spots in the sample with a 50x air objective (NA= 0.75), 10% laser power (~1.3 mW), 10s exposure time and 1 accumulation.



Figure S4 - Extended pyridine SERS measurement confirming that CTAB was removed after washing the mesoporous silica coated AuNRs (Au@SiO₂), whereas CTAB is clearly detected for non-coated, CTAB stabilized AuNRs. Raman spectra were recorded with a 50x air objective (NA= 0.75), 1% laser power (~0.14 mW), 1s exposure time and 1 accumulation.



Figure S5 – The size of the supraparticles depends on the size of the emulsion droplets. Light microscopy images of the emulsion droplets prepared by mixing 100 μ L H₂O and 5.0 mL hexadecane with 1 wt% SPAN80 with a Turrax mixer using a mixing speed of a) 6000, c) 12000 or e) 18000 rpm. b,d,f) SEM images and corresponding size distribution of supraparticles originating from the a) 6000, c) 12000 and e) 18000 rpm emulsions.



Figure S6 - Assembly of uncoated, CTAB-stabilized AuNRs renders a mixture of supraparticles and non-assembled AuNRs. High-angle annular dark-field (HAADF) and secondary electron (SE) images of the resulting supraparticles are shown. A substantial number non-assembled NRs were observed due to the destabilizing effect of CTAB on the emulsion and Van der Waals attractions between the NRs.



Figure S7 – Plasmonic coupling between NRs upon assembly in supraparticles. VIS-NIR spectra of the non-etched & etched Au@SiO₂ NRs in methanol and its respective supraparticles in hexadecane.



Figure S8 – Plasmonic coupling between thin silica coated AuNRs when assembled in supraparticles. The VIS-NIR spectra show the longitudinal LSPR of the single 5 nm thin silica coated AuNRs (black) in ethanol, and that of the self-assembled 5 nm (light blue) and 7 nm coated Au@SiO₂ NR supraparticles in hexadecane (dark blue).



Figure S9 - **Extended pyridine SERS measurement** confirming that no organics (CTAB, SPAN80, hexadecane) were present after washing the mesoporous silica coated AuNRs (Au@SiO₂) supraparticles, and that the AuNR surface was accessible for the pyridine probe molecules. Raman spectra were recorded with a 50x air objective (NA= 0.75), 1% laser power (~0.14 mW), 1s exposure time and 1 accumulation.



Figure S10 - SERS performance of different batches of mesoporous silica coated AuNR supraparticles (d_{shell} = 18 nm). The Raman measurements were recorded with a 633 nm laser, 0.07 mW laser power, 50x air objective (NA= 0.75, spotsize ~1 µm), 1s exposure time and 1 accumulation per spot.



Figure S11 - SERS performance of supraparticles containing Au@SiO₂ NRs with a different silica shell thickness. a) Raman spectra of crystal violet on supraparticles consisting of Au@SiO₂ NRs with d_{shell}= 3 (red), 18 (orange) and 35 nm (blue) and d_{pore}= <1, 2.5 and 4-5 nm, respectively. b) The maximum intensity between 1616 and 1618 cm⁻¹ as a function of the shell thickness. The Raman measurements were recorded with a 633 nm laser, 0.07 mW laser power, 50x air objective (NA= 0.75, spotsize ~1 μ m).



Figure S12 - Reproducible SERS measurement spectra of crystal violet in the presence of non-assembled a) nonetched Au@SiO2 NR and b) etched Au@SiO2 NR measured at 10 different spots in each capillary. The Raman measurements were recorded with a 633 nm laser, 0.14 mW laser power, 50x air objective (NA= 0.75, spotsize ~1 μ m), exposure time of 1s and 100 accumulations at each spot



Figure S13 - SERS measurement spectra of crystal violet in the presence of a) non-etched Au@SiO₂ NR SPs and b) etched Au@SiO₂ NR SPs measured at 6 different spots on Si-wafer. The Raman measurements were recorded with a 633 nm laser, 0.14 mW laser power, 50x air objective (NA= 0.75, spot size ~1 μ m), exposure time of 1s and 100 accumulations at each spot.



Figure S14 – SERS performance with differently sized supraparticles containing non-etched (a) and etched (b) Au@SiO₂ NR SPs. Histogram of the peak intensity of SERS spectra of crystal violet between 1616 - 1618 cm⁻¹ measured with a) etched and b) nonetched Au@SiO₂ NR SPs at 6 different spots and its corresponding SEM image. The Raman measurements were recorded with a 633 nm laser, 014 mW laser power, 50x air objective (NA= 0.75, spotsize ~1 μ m), exposure time of 1s and 100 accumulations.

Raman Signal (cm ⁻¹)	Peak Assignment
792	C-H out of plane bending
914	Ring skeletal vibration
1178	C-H in plane bending
1370	N-phenyl stretching
617	C-C stretching

Table S1 – List of vibrations modes of Crystal Violet