Supporting Information:

The Conquest of Middle-Earth: combining top-down and bottom-up nanofabrication for constructing nanoparticle based devices

Yuri A. Diaz Fernandez,^{*a c*} Tina A. Gschneidtner,^{*a*} Carl Wadell,^{*b*} Louise. H. Fornander,^{*a*} Samuel Lara Avila,^{*b*} Christoph Langhammer,^{*b*} Fredrik Westerlund,^{*a*} and Kasper Moth-Poulsen^{*a*}*

^{*a*} Department of Chemical and Biological Engineering, Chalmers University of Technology, SE-412 96 Gothenburg, Sweden. email: kasper.moth-poulsen@chalmers.se

^b Department of Applied Physics, Chalmers University of Technology, SE-412 96 Gothenburg, Sweden.

^c Current address: Open Innovation Hub for Antimicrobial Surfaces, Surface Science Research Centre, Department of Chemistry, University of Liverpool, Liverpool L69 3BX, UK

Contents:

- SI1 Experimental section
- SI2 SEM images of Au cubic NP sub-monolayers
- SI3 SEM images of Au rhombic dodecahedral NP sub-monolayers
- SI4 Stability of NP sub-monolayers after acetone rinsing
- SI5 TEM images of Pd cubic NPs
- SI6 References for SI

SI1 Experimental section

Instruments

SEM: Ultra 55 FEG SEM, Zeiss operated at 10 kV.

TEM: JEOL JEM-1200EX II

Centrifuge: Eppendorf Mini Spin rotor KL125 (9 cm)

Fluorescence Microscope : Epi-fluorescence microscope (Zeiss AxioObserver.Z1) equipped with a Photometrics Evolve EMCCD camera and a 100x oil immersion TIRF objective (NA=1.46) from Zeiss.

Liposome Extruder: Mini-Extruder, Avanti

Plasma Cleaner: Plasma Therm Batchtop RIE 95m

E-beam Evaporation System: Lesker PVD 225 Evaporator

Reagents

All starting materials for the synthesis of the NPs were purchased from Sigma-Aldrich, and used as received. Sodium 2-mercaptoethanesulfonate (MESNa) was also purchased from Sigma-Aldrich. Poly(methyl methacrylate) solution 4% by weight in anisole (MCC NANO 950k PMMA A4) was used as received.

Pd and Au nanoparticles of different sizes and shapes were synthetized adapting procedures previously described in the literature,^{1–3} and detailed below.

All particles were used fresh, since occasionally sedimentation was observed after several hours. However re-dispersion lead to colloidal solutions, where no reshaping or ripening was reveal by TEM inspection.

For the preparation of the liposome solutions, the lipids were dissolved in chloroform (5 mg/ml) and mixed to a final proportion of 99% POPC lipids (1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine, Avanti Polar Lipids, Inc.) and 1% Rh-DHPE lipids (Lissamine[™] Rhodamine B 1,2-Dihexadecanoyl-sn-Glycero-3-Phosphoethanolamine, Invitrogen[™] Life Technologies). A thin dried lipid film was formed in a rotavapor at low vacuum, followed by a couple of hours drying at higher vacuum. The dried film was vigorously rehydrated in buffer (100 mM NaCl, 10 mM Tris, 10 mM Boric Acid, 0.225 mM EDTA pH 8.0), followed by 5 cycles of freezing in liquid N2 and thawing at 37°C. This stock solution can be stored in the freezer for a couple of months. The liposomes were then formed by extruding 51 times through a polycarbonate filter with pore size diameter of 100 nm (by Avanti mini-extruder).

<u>Au cube (50 nm):</u>

Au nanocubes were synthesized with a method described previously, and the concentration of NPs was estimated to be $c_{NP} \approx 1.77 \cdot 10^{11}$ NP/ml.¹ Two post-synthesis centrifugation (6000 rpm, 10 min) and re-dispersion (deionized water) steps led stable colloids at room temperature. The remaining CTAC concentration was 5.8 μM .

<u>Pd cube (20 nm):</u>

Pd 20 nm cubes were synthesized as described elsewhere.² The NP concentration was estimated to be $c_{NP} \approx 8.14 \cdot 10^{11}$ NP/ml. Colloidal solutions were store as synthetized at 30°C and used fresh. Two post-synthesis centrifugation (8000 rpm, 10 min) and re-dispersion (deionized water) steps reduced the CTAB concentration to a final value of 3 μ M.

Au rhombic dodecahedral (50 nm):

Au rhombic dodecahedra were synthesized as described previously.¹ The NP concentration was estimated to be $c_{NP} \approx 6.63 \cdot 10^{10}$ NP/ml. Two post-synthesis centrifugation (8000 rpm, 10 min) and re-dispersion (deionized water) steps reduced the CTAB concentration to a final value of 5.8 μ M.

Fabrication of nanostructured surfaces

Au disks were fabricated onto Si substrates by standard hole-mask colloidal lithography (HCL) as described in before.⁴ The mask was made using 120 nm polystyrene beads (PS, sulfate latex, Interfacial Dynamics Corporation). The disks are formed by evaporating 5 nm Cr followed by 30 nm Au through the HCLmask in a Lesker PVD 225 Evaporator, base pressure of 5 \times 10⁻⁷ Torr, at an evaporation rate of 1 Å/s. The mask was subsequently removed using acetone. Gold nanowires were patterned on thermally oxidized Si substrates using standard electron beam (e-beam) lithography followed by metal lift-off. Oxidized silicon substrates (400 nm SiO2) were cleaned using acetone, isopropanol, water and oxygen plasma etching (50 W, 250 mbar, 10sccm of 02) for 3 min. An ebeam resist bilayer (100nm PMMA/ 60 nm ZEP 520 A) is spin coated on cleaned substrates, patterned using a current of 1 nA with a dose of 750 uCcm-2 in a JEOL-9300FS e-beam lithography system. Resist is developed for 20 s in Oxylene and 1 min 30 sec in a mixture of isopropanol/ water (93%/7% v/v). Following development, resist residuals are removed from developed areas using the same oxygen plasma treatment for 30 s; then, 30 nm of gold are evaporated using 5 nm of titanium as sticking layer. The process is completed with overnight metal liftoff in acetone followed by rinsing in isopropanol and water, and blow-dried using N2.

Preparation of NP sub-monolayers

The oxidized Si substrates or the nanofabricated Au-Si surfaces were oxygenplasma cleaned before use. A PMMA pool was built-up on the edge of the 1 cm x 1 cm wafers by deposition of the viscous PMMA A4 solution on the substrate, and baking at 140°C for 5 min in a hot plate. The baking step was not essential, but provided further mechanical resistance to the pool. The available surface within the pool was first rinsed with deionized water and then with the relevant buffer solutions. The rinsing procedure was performed by continuous exchange of solutions within the PMMA pool, using simultaneously drain and source pipettes tips. Several rinsing cycles were allowed between different functionalization steps, and the continuous flow during exchange of solutions prevented the drving of the surface. The functionalization of Au nanofabricated surface with MesNa was achieved by incubation of the surface at room temperature for two hours in contact with 6•10⁻⁵ M solution of MESNa in deionized water. When required, the lipids bilayers were formed by introducing the liposome solutions in the pool, allowing 15 min of equilibration. The formation of homogeneous lipid bilayers was monitored with the fluorescence microscope using fluorescent labeled lipids. The colloidal solutions, prepared as described above, were incubated on the surface at room temperature for 30 min, leading to homogeneous NP sub-monolayers on clean oxidized Si surfaces. During all

incubation steps, the samples were kept in a closed environment to avoid evaporation of the solution. For every batch of surfaces and NP solutions, a control sample of clean oxidized Si was also prepared. The substrates with the self-assembled NP sub-monolayers were plasma cleaned and characterized by SEM. Quantitative analysis of the images was performed using ImageJ 1.46r.

Figure S1 Schematic representation of the self-assembly of metal NPs submonolayers on oxidized Si surfaces (S1.1a-d) and on lipid-bilayer passivated surfaces (S1.2a-d).



SI2- Representative SEM images of Au cubes (average size 50 nm) on clean oxidized Si surfaces. Different magnifications



SI3 Representative SEM images of Au rhombic dodecahedra (average size 50 nm) on clean oxidized Si surfaces. Different magnifications



SI4 Representative SEM images of Pd cube (average 25 nm) on clean oxidized Si surfaces after rinsing with acetone . Different magnifications



SI5 Representative TEM images of Pd cube (average size 25 nm) after two centrifugation/re-dispersion cycles, showing the inter-particle gaps that demonstrate the absence of ripening during the removal of the excess of surfactant.



SI-6: References for supporting information

- Wu, H.-L.; Kuo, C.-H.; Huang, M. H. Seed-Mediated Synthesis of Gold Nanocrystals with Systematic Shape Evolution from Cubic to Trisoctahedral and Rhombic Dodecahedral Structures. *Langmuir* 2010, *26*, 12307–12313.
- (2) Niu, W.; Li, Z.-Y.; Shi, L.; Liu, X.; Li, H.; Han, S.; Chen, J.; Xu, G. Seed-Mediated Growth of Nearly Monodisperse Palladium Nanocubes with Controllable Sizes. *Cryst. Growth Des.* **2008**, *8*, 4440–4444.
- (3) Niu, W.; Zhang, L.; Xu, G. Shape-Controlled Synthesis of Single-Crystalline Palladium Nanocrystals. *ACS Nano* **2010**, *4*, 1987–1996.)
- (4) Fredriksson et al. Advanced Materials, 2007, 19, 4297-4302