

Electronic Supplementary Information

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Instrumentation

For optical microscopy imaging an Olympus CKX 41 microscope was operated with an Olympus XC 30 camera. Data processing was carried out with the software OLYMPUS Stream Start 1.8. Images were taken at 20-fold magnification with an exposure time of 50 ms. Dynamic light scattering (DLS) measurements were carried out on a Nano ZS Zetasizer (Malvern Instruments Ltd., Worcestershire, UK) in disposable semi-micro PMMA cuvettes (BRAND GmbH & Co. KG, Wertheim, Germany) with a path length of 1 cm. AFM measurements were performed using a Nano Wizard (JPK Instruments AG) in tapping mode under air on silicon surfaces. XPS analyses of surfaces were done with a Kratos Axis Ultra (Kratos) using monochromated Al K α irradiation with an excitation energy of 1486.6 eV. For region scans a pass energy of 0.02 eV was employed. The obtained data were analyzed with CasaXPS Software Suite v2315. All spectra were calibrated to the binding energy of the C-1s-orbital in aliphatic carbon-carbon chains (285 eV). Resistance measurements were performed using a Uni-T True RMS Digital Multimeter UT139C. All chemicals were purchased from Acros Organics, Fischer Scientific GmbH, Schwerte, Germany, Aldrich, Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany and Alfa Aesar, Alfa Aesar GmbH & Co KG, Karlsruhe, Germany and used without further purification.

Preparation of poly(dimethyl siloxane) (PDMS) stamps

PDMS stamps were prepared from Sylgard 184 provided by Dow Corning. PDMS and curing agent were mixed in a ratio of 10:1 and stirred for 10 min by hand. The mixture was poured onto a structured silicon waver a cured at 80°C overnight. After removing the PDMS from the silicon waver the structured stamps were cut out with a scalpel and treated for 55 min with a UV ozonizer (PSD-UV, Novascan Technologies Inc.). If not used immediately, the PDMS stamps were stored in deionized water.

Preparation of 11-hydroxyundecyl silane SAMs

Glass or silicon surfaces were cut into pieces of 14 x 14 mm. The pieces were sonicated in pentane, acetone and deionized water for 3 min each. Then they were immersed into a freshly prepared solution of piranha ($\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2 - 3/1$) and stirred for 30 min, before they were extensively washed with deionized water and dried under an argon stream. The clean and dry surfaces were immersed in a freshly prepared solution of 11-acetoxytrichlorosilane (0.1 vol%) in toluene (20 ml) for 1 h. Afterwards the surfaces were washed with dichloromethane, ethanol and deionized water. After drying they were placed in an HCl-solution (2.5 mM) at 85 °C for another 2 h and washed again with deionized water.

Preparation of octadecyl silane SAMs

Glass or silicon surfaces were cut into pieces of 14 x 14 mm. The pieces were sonicated in pentane, acetone and deionized water for 3 min each. Then they were immersed into a freshly prepared solution of piranha ($\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2 - 3/1$) and stirred for 30 min, before they were extensively washed with deionized water and dried under an argon stream. The clean and dry surfaces were then immersed in a freshly prepared solution of octadecyltrichlorosilane (0.1 vol%) in toluene (20 ml) for 1 hour. Afterwards the surfaces were washed with dichloromethane, ethanol and deionized water.

Preparation of TiO_2 nanoparticles

A 100 ml three-necked flask was filled with diethylene glycol (60 ml) under argon atmosphere and heated up to 60 °C. TiCl_4 (2 ml) was added and the solution was heated to 75°C. Then H_2O (1 ml) was added and the whole mixture was stirred for 3 h at 160°C. After cooling down to room temperature the suspension was transferred into a beaker and acetone (100 ml) was added. The mixture was centrifuged for 10 min at 3500 rpm. The supernatant was decanted and the TiO_2 -Nanoparticles were washed further three times with acetone (35ml). The remaining solvent was removed under reduced pressure. The DLS measurements showed a hydrodynamic diameter of 3-5 nm and a *zeta*-potential of -33 mV.

Microcontact printing

The ink solution was prepared by adding TiO₂ NPs (5 mg) to methanol (1 ml) in a small GC-vial and sonicated for 5 min. After that time ethanolamine (3 μl) was added and the solution was sonicated for 1 min. The freshly prepared ink solution (30 μl) was placed on a freshly oxidized PDMS stamp for 30 s to 2 min of incubation. The stamp was then dried with an argon stream before it was placed on an 11-hydroxyundecyl silane SAM or an octadecyl silane SAM. The stamp was pressed gently to the surface. After reaction times from 5 s to 30 min the stamp was removed and the surface was extensively washed with dichloromethane, ethanol and deionized water before they were used for further functionalization.

Formation of metal nanoparticles inside the TiO₂ nanoparticle aggregates

The in situ nanoparticle formation on the surface was carried out by adding the structured surfaces in an aqueous solution of metal salt (HAuCl₄, FeSO₄, AgNO₃, Cu(OAc)₂, 0.6 M, 20 mL) for 45 min. After that time a NaBH₄ solution (0.1 M, 1 mL) was added drop wise over 1 h, before the surfaces were rinsed with deionized water and ethanol.

Electroless deposition of Cu

Cu micro wires were prepared by incubation of Au NPs containing TiO₂ NP patterns in a freshly prepared electroless deposition solution (CuSO₄ x 5H₂O (32 mM), triethanolamine (0.24 M), ethylenediamine tetraacetic acid (EDTA) (37 mM), dimethylaminoborane (67 mM) and water (20 mL) at a pH of 10.67) for 9 min. The surfaces were sonicated with deionized water and ethanol.

Resistivity of the Cu wires

$$R = \rho * \frac{l}{A} \quad \leftrightarrow \quad \rho = R * \frac{A}{l}$$

$$R = 2.8 \, \Omega$$

$$l = 0.1 \, \text{m}$$

$$A = 0.0005 \, \text{mm}^2$$

$$\rho = 2.8 \, \Omega * \frac{0.0005 \, \text{mm}^2}{0.1 \, \text{m}} = 0.014 \, \Omega * \text{mm}^2 * \text{m}^{-1}$$

Additional experimental data

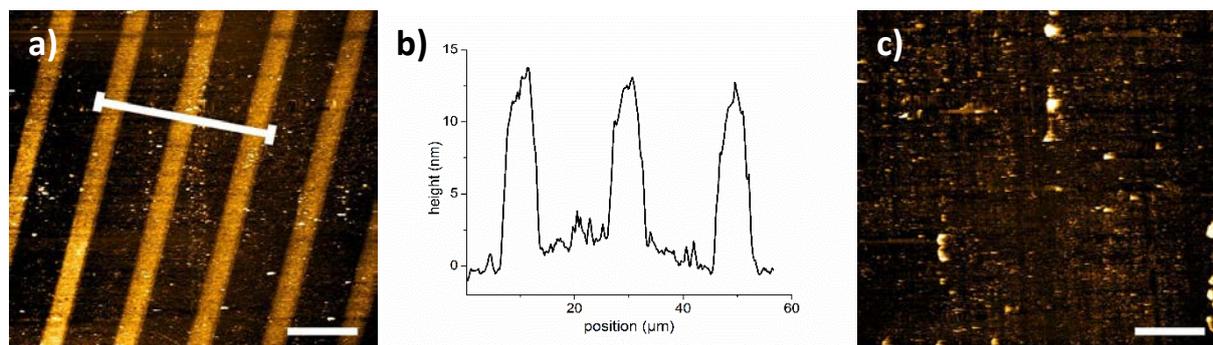


Figure 1S: a) AFM image of a patterned surface printed with an ink solution containing ethylenediamine as a cross linker. b) Corresponding height profile to AFM image of a). c) AFM image of a patterned surface printed with an ink solution containing ethylene glycol as a cross linker. Scale = 20 μm.

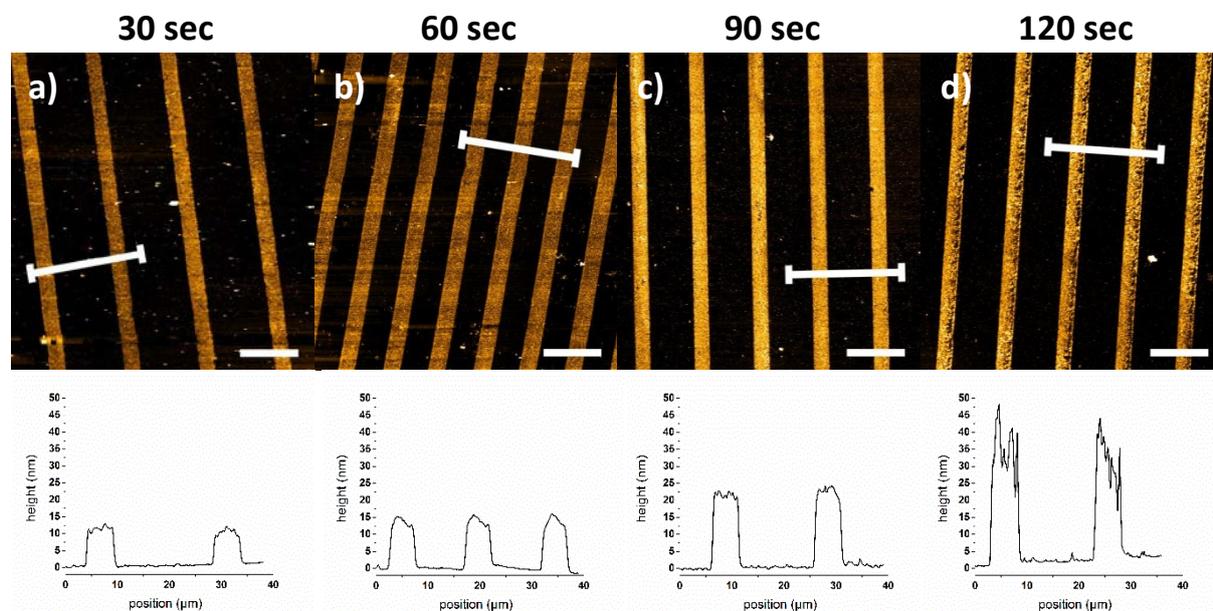


Figure 2S: AFM images and height profiles of patterned surfaces after printing for 5 min and different incubation times. a) Incubation time of 30 s. b) Incubation time of 60 s. c) Incubation time of 90 s. Incubation time of 120 s. Scale = 20 μm.

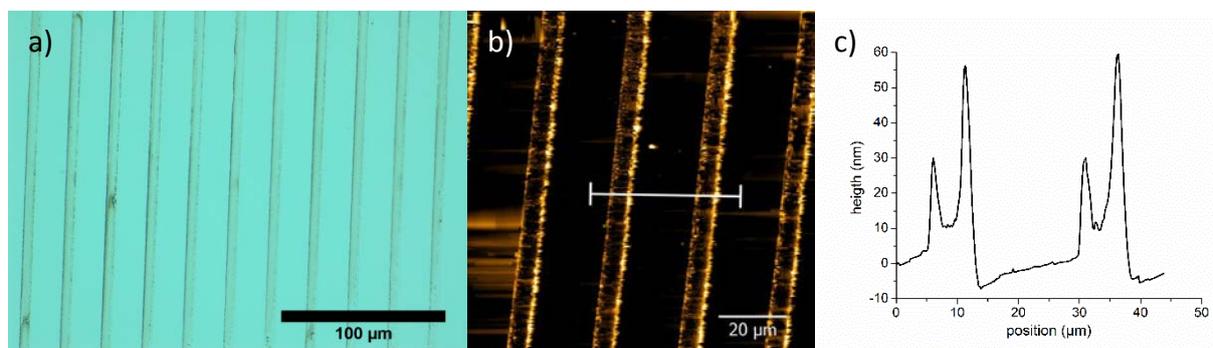


Figure 3S: a) Microscopic picture of surface printed with a heightened concentration (25 mg TiO₂ NP, 15 μL ethanolamine). b) AFM measurement of the same surface of a) with corresponding height profile c).

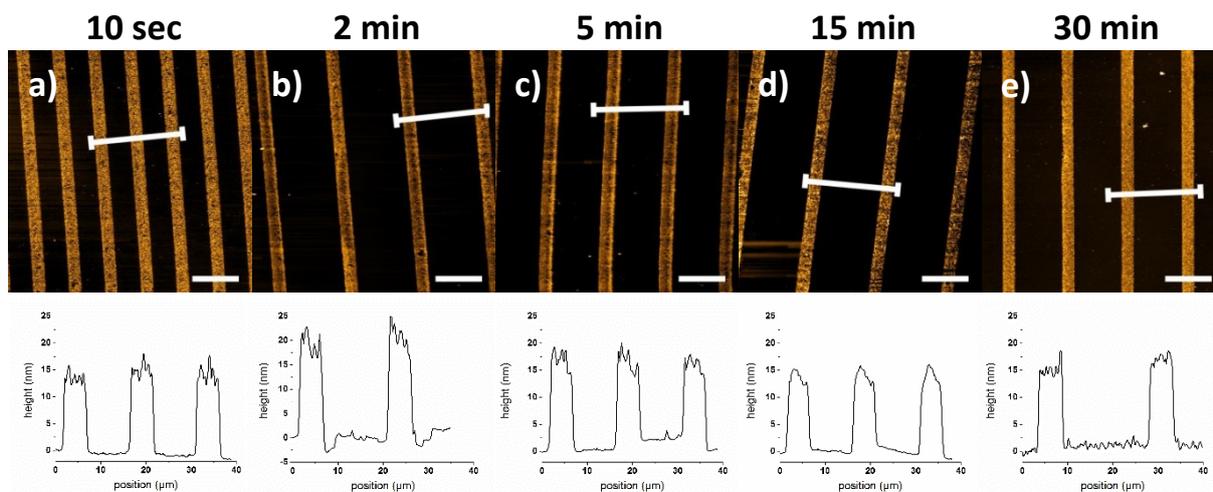


Figure 4S: AFM images and height profiles of patterned surfaces after printing with different printing times. a) Printing time of 10 sec. b) Printing time of 2 min. c) Printing time of 5 min. d) Printing time of 15 min. e) Printing time of 30 min. Scale = 20 μm .

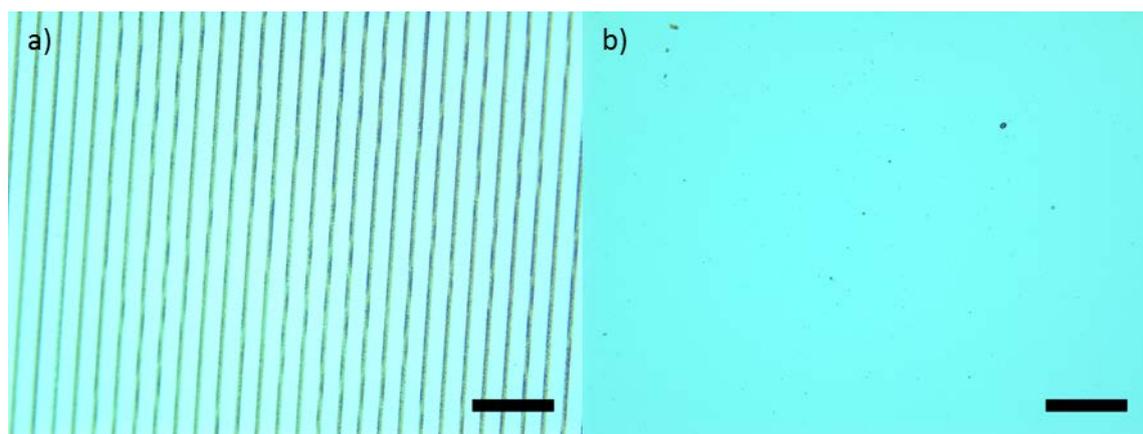


Figure 5S: a) Activated silicon surface with free silanol groups patterned with TiO_2 NPs and ethanolamine. b) Octadecyl-SAM printed with same solution of TiO_2 NPs and ethanolamine as in a). Scale = 100 μm .

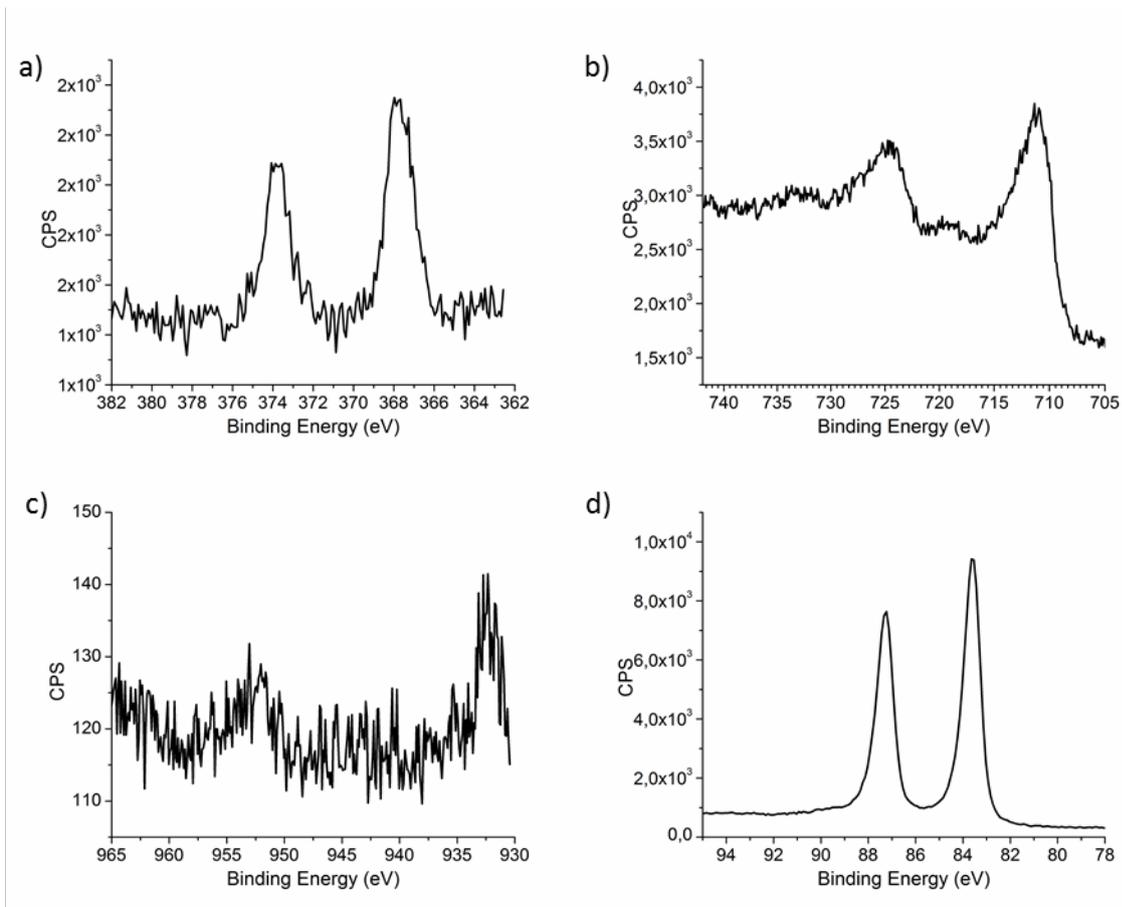


Figure 6S: XPS measurements of different metals absorbed into the TiO_2 NP patterns. a) XPS signal of the Ag 3d signal (left Ag 3d 3/2 and right Ag 3d 5/2). b) XPS signal of the Fe 2p signal (left Fe 2p 1/2 and right Fe 2p 3/2). c) XPS signal of the Cu 2p signal (left Cu 2p 1/2 and right Cu 2p 3/2). d) XPS signal of the Au 4f signal (left Au 4f 5/2 and right Au 4f 7/2).

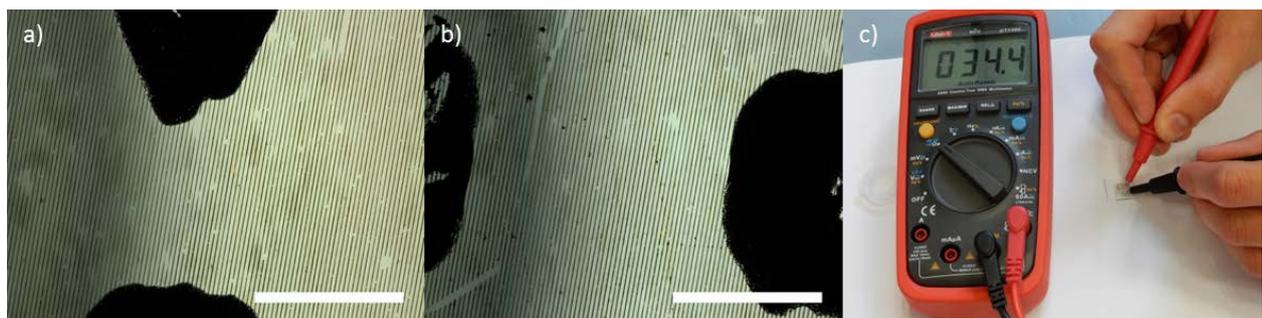


Figure 7S: Light microscopic picture of a) silver droplets placed in parallel direction to the pattern, b) silver droplets placed in orthogonal direction to the pattern. c) Picture of the resistance measurement in parallel direction. Scale = 200 μm .