Electronic Supplementary Information

Direct modification of colloidal hole-masks for locally ordered heteroassemblies of nanostructures over large areas

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Experimental

Materials

PMMA ($M_W = 495,000, 4\%$ in anisole) was purchased from Micro resist technology GmbH (Germany). Poly(diallyldimethylammonium chloride) (PDDA, $M_w 200,000-350,000 20\%$ in H₂O) and poly(sodium-4styrenesulfonate) (PSS, $M_w 70,000, 30\%$ in H₂O) were purchased from Sigma-Aldrich (Denmark). Polyammonium chloride (PAX-XL60) was purchased from Kemira Miljø (Denmark). Polystyrene (PS) sulfate latex particles (164 nm, 4.3% coefficient of variation, 8.0 per cent solids (w/v) were purchased from Invitrogen (Denmark).

Hole-mask fabrication

Silicon substrates were sonicated for 30 min in acetone and glass substrates were wiped with acetone. The substrates were then cleaned for 10 min in oxygen plasma (Vision 300 MK II, Advanced Vacuum) at a RF power of 150 W, 55 sccm oxygen flow and 300 mbar pressure. A sacrificial PMMA layer was spin coated on the substrates by flooding the substrates and immediately after spun at 3000 rpm. The substrates were baked on a hotplate for two minutes at 180°C. PS particles were deposited on the PMMA coated substrates after 5 min of UV ozone (UV/Ozone ProCleanerTM Plus from Bioforce Nanosciences) by a colloidal lithography procedure

reported elsewhere.¹ In brief: Three layers of polyelectrolytes (PDDA 2% in MQ water, PSS 2% in MQ water, PAX-XL60 5% in MQ water; all by weight) were sequentially adsorbed on the PMMA for 30s followed by rinsing in MQ water (30s) and drying under nitrogen gas. The Polystyrene particles (0.2% in MQ water by weight) were allowed to self-assemble onto the surface for 2 min followed by 1 min rinsing in MQ water to remove excess particles and the samples were dried using nitrogen gas.

An oxygen plasma etch resistant mask of 20 nm titanium was evaporated onto the patterns by electron beamstimulated thermal evaporation physical vapour deposition (prototype system from Polyteknik, Denmark). To assist better adhesion between the titanium and the PMMA surface ion beam assisted deposition (IBAD) was performed for the first five seconds of the evaporation. The particles were tape stripped off the samples and the samples were treated for 10 minutes in oxygen plasma (Vision 300 MK II, Advanced Vacuum) at a RF power of 50 W, 40 sccm oxygen flow and 25 mbar pressure to selectively remove the PMMA layer under the holes.

Mask modification and fabrication of structures

The hole-masks were modified by oblique angle deposition (OAD) of titanium. The evaporations were performed at an angle of 70° to the substrate surface normal and at a rotation speed of 5 rpm. The distance between the samples and the target was 51 cm for the mask modification and all subsequent depositions of structures. Tilt and rotation depended on the given structure. The layer thicknesses stated are not corrected for the tilt of the sample compared to the thickness monitor. All tilt angles stated are with respect to the substrate surface normal. The lift off step was performed by thoroughly rinsing with acetone followed by rinsing in isopropyl alcohol (IPA).

Scanning electron microscopy (SEM)

SEM images were acquired using a Magellan 600 from FEI. The microscope was operated at a working distance of approximately 4 mm (some side view images were acquired at 5 mm), an acceleration voltage of 5kV and a

nominal probe current of 50 pA. Samples on silicon substrates were imaged without further processing while glass samples were covered in a 5 nm thick titanium film to avoid charging.

UVVis

Extinction data from samples on glass substrates were measured using a Shimadzu UV-3600 UV-VIS-NIR spectrophotometer. Dual beam measurements were performed with a clean glass slide as reference. The extinction data for each sample was normalized to the highest extinction value.



Figures and optical properties

Figure S1: Schematic representation of the fabrication steps for all the structures presented in the work. 1: Varying the size of a single disk. 2: Disk dimers with systematically varied size ratios. 3: Gold dimer with a titanium disk in the gap. 4: Symmetrically stacked, two-chemistry system. 5: Asymmetrically stacked two-chemistry system. 6: Chiral structures



Figure S2: The measured disk sizes versus modification layer thickness. On the order of 800 individual structures were measured on SEM images from three different areas on each sample to generate each data points. Error bars = standard error of the mean



Figure S3: Optical properties of gold nanodisks on silica supports. The top row shows SEM images of the samples presented in the main paper. The normalized extinction spectra of the four samples are presented in the graph. The colour code and symbols of the graphs are correlated to those of the SEM images.

The optical properties of the gold nanodisks on silica disk support samples (shown in Figure 3 in the main paper) were investigated experimentally through extinction measurements. Gold nanostructures support localised surface plasmon resonances (LSPRs) making their optical properties highly interesting and useful in many applications. The spectral position of an LSPR is dependent on the size, shape, material and local dielectric environment of the supporting nanostructure.² Normalized optical extinction spectra of the four different samples recorded in air are shown in Figure S3 along with SEM images of the corresponding samples, as indicated by the colour code and geometric symbols. All samples show one LSPR peak in the visible range. It is observed that the

LSPR peak shifts to shorter wavelengths as the gold disk diameter is decreased while the height and the dielectric environment are kept constant, as expected from literature.³ Interestingly a shift of the gold disk laterally with respect to the silica disk resulted in a blue shift of the LSPR compared to the centred disks of the same size (Figure S3 comparing the full line marked by an circle and the dashed line marked by a triangle). The blue shift can be qualitatively understood in terms of a change in the distribution of the substrate dielectric around the nanostructure which then fills a smaller part of the LSPR near field. Tuning the dielectric environment in the near field of an LSPR is a topic of current interest and has been used to increase LSPR refractive index sensitivity.⁴⁻⁵

References

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