High-yield and high-precision nanoparticle assembly: towards complex plasmonic antennas

Valentin Flauraud [a], Massimo Mastrangeli [b], Elmira Shahrabi [a], Jürgen Brugger [a]

[a] Microsystems Laboratory - EPFL, Lausanne, 1015 Switzerland
[b] Bio, Electro And Mechanical Systems – Université Libre de Bruxelles, Bruxelles, 1050 Belgium
e-mail: valentin.flauraud@epfl.ch

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Capillarity assisted particle assembly (CAPA) (Fig. 1) makes use of the receding motion of a confined colloidal solution to selectively place nanoparticles (NPs) onto predefined locations of a template substrate [1]. The process is fast, parallel and scalable to large substrate areas. It enables positioning colloids with material and geometric properties unachievable by thin film processing. CAPA is particularly suited to the placement of gold nanospheres [1-2] and nanorods [3] both at single-particle [1, 3] and multimer level [2]—nanostructures with wide-ranging applications in plasmonics [4]. High NP assembly yield and precision are central for this. The yield of CAPA is very sensitive to the accumulation of NPs at the moving triple contact line (Fig 2), which can be optimized by tailoring the contact line velocity, substrate temperature and receding contact angle [3]—all affecting the flow field in the liquid meniscus (Fig 1). Filling yield also increases for larger nanotraps. This however compromises NP placement precision [2-3].

We present a high-confinement approach to CAPA enabling both high-precision and high-yield assembly of single NPs and of multi-particle clusters into silicon and glass substrates. The template substrates are processed using electron beam lithography, reactive ion etching and surface-chemical functionalization (Fig. 3). The resulting nanotraps have vertical sidewalls and uniform cross-sections. For single NPs, the nanotraps are patterned with diameters only slightly larger than that of a single particle to hinder multiparticle placement (Fig. 4). Larger capture areas correlated with higher assembly yield at the expense of reduced control and reproducibility of final NP placement within the traps. This was particularly evident for nanorods, whereby wider traps showed higher assembly yields yet broader angular dispersion. In view of functional plasmonic nanoantennas we present two fabrication approaches for the assembly of ordered clusters of tightly packed NPs. The first relies on high-resolution definition of cluster geometry composed by adjacent and closely spaced single NP traps (Fig. 4a). In the second approach, NPs are assembled in single traps allocating predefined clusters with interparticle nanogaps (Fig. 4b). This imposes challenging constraints on trap dimensions to obtain predefined counts and relative positioning of NPs. We demonstrated high-yield assembly of tightly confined gold nanospheres and nanorods by inducing high NP accumulation at the receding contact line of the meniscus with receding contact angles below 45° (Fig. 2b) and contact line velocities lower than 1 µm/s. Optimal assembly conditions were determined from yield analysis over large substrate areas by optical and electron microscopy, as well as through the analysis of the NP accumulation zone upon drying of the solution after assembly (Fig. 2c-d). Setting the substrate temperature at 20 to 25° C above the dew point allowed both high NP density and sufficient horizontal drag force at the contact line for selective and non-convective assembly. The formation of liquid crystal domains at the contact line confirmed the tight packing of the rods [3]. Areas with 400 single 40 x 120 nm Au nanorods were analysed revealing an unprecedented angular distribution with standard deviation below 2° and yield above 85% (Fig. 5). In the case of nanoparticle clusters, spherical Au colloids of 50 nm in diameter were successfully assembled at 93% yield for areas including over 2000 structures (Fig 6).

The presentation will include full information on background and plasmonic applications of CAPA, template design and fabrication and analysis of performance of the assembly method.

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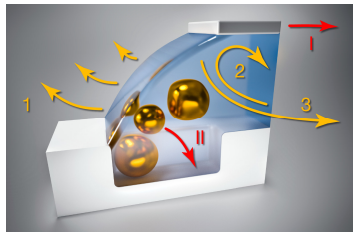

Figure 1. Schematic of CAPA. Yellow: the three main flows driving the NP's rising from (1) evaporation (2) non-slip condition and (3) diffusion. Red: top slide (I) and NP motion (II).

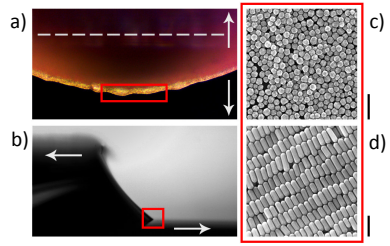

Figure 2. Top (a) and side (b) views of receding meniscus (slide-to-substrate gap: 800 µm) with NP accumulation during CAPA, and SEM pictures (scale bars: 200 nm) of spheres (c) and rods (d) packed at the contact line upon drying.

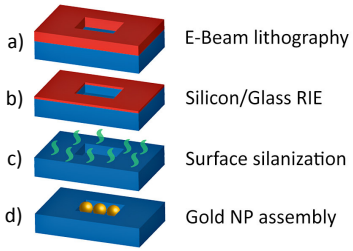

Figure 3. Nanoprocessing of template substrate. (a) e-beam lithography of positive tone resist, (b) reactive ion etching of substrate, (c) surface silanization, (d) NP placement by CAPA.

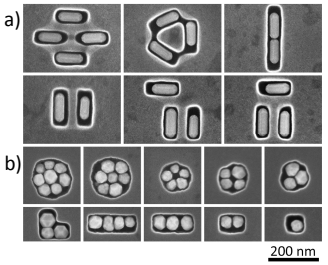

Figure 4. Highly confined nanoparticle clusters in silicon nanotraps by CAPA. (a) 40 x 120 nm Au nanorods, (b) 50 nm Au nanospheres.

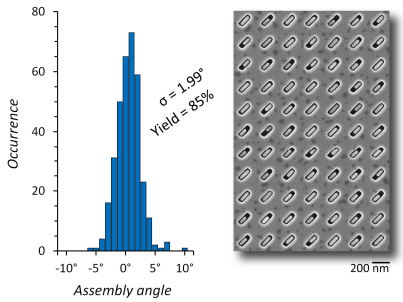

Figure 5. Angular distribution of a 400 nanorod assembly (a subset is shown). Standard deviation is smaller than 2°.

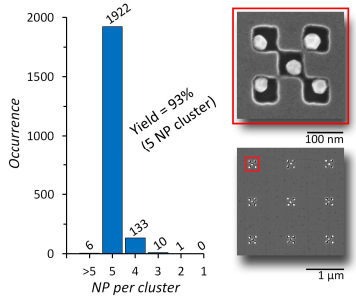

Figure 6. Assembly yield histogram for 2072 checkerboard clusters hosting five individual 50 nm Au NPs (see insets).