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Facile Formation of Ordered Vertical Arrays by Droplet Evaporation of Au Nanorod Organic Solutions

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Supplementary information

Synthesis of Au Nanorods

Seed Solution

CTAB solution (5 mL, 0.2 M) was mixed with 5.0 mL of 0.5 mM $HAuCl_4$. To the stirred solution 0.6 mL of ice-cold 0.01 M $NaBH_4$ was added, which resulted in the formation of a pale brown solution. Vigorous stirring of the seed solution was continued for 2 min. Solution was kept at 30 °C until further use.

Growth of Nanorods (14 × 44 nm)

CTAB (12.5mL, 0.2 M) was added to 0.7 mL of 4 mM of $AgNO_3$ at 30 °C. To this solution, 25 mL of 1 mM $HAuCl_4$ was added, and after gentle mixing 0.35 mL of 0.0788 M ascorbic acid

was added. Upon addition of ascorbic acid the solution color changed from intense orange to colorless. Finally, 35 μL of seed solution were added at 30 °C. The color of the solution gradually changed from colorless to intense red (10-20 min). The solution was stirred at 30 °C until growth process was complete (90-120 min). The final mean size of obtained nanorods was 14 ± 2 nm × 44 ± 3 nm.

Overgrowth of Nanorods (23 × 55 nm)

Nanorods 23 × 55 nm were obtained by overgrowth of previously synthesized nanorods (14×44 nm). Specifically, 0.0788 M ascorbic acid was added dropwise (5 μL/5 min) to 15 mL of nanorod solution previously synthesized. Growth rate was monitored by measuring solution UV-Vis spectra every 4/5 ascorbic acid additions. Ascorbic acid was added until no spectroscopic changes were detected (ca. 15 additions). Figure S1 shows SEM images of nanorods obtained by overgrowth of different size nanorods. The final nanorod mean sizes were the following: a) 23 ± 3 nm (diameter) × 55 ± 3 nm (length) aspect ratio (AR) = 2.3; b) 19 ±2 × 49 ±3, AR = 2.6; c) 19 ±2 × 60 ±3. AR = 3. Figure S1c shows the corresponding UV-vis spectra of nanorods a-c with maxima longitudinal peaks at 2,3, 2.6, 3.1, respectively. Nanorods of increasing aspect ratios were obtained by increasing the volume of $AgNO_3$ added to the growth solution, specifically 0.7ml for A.R 2.3, 1ml for A.R.2.6 and 1.3 ml for A.R.3.

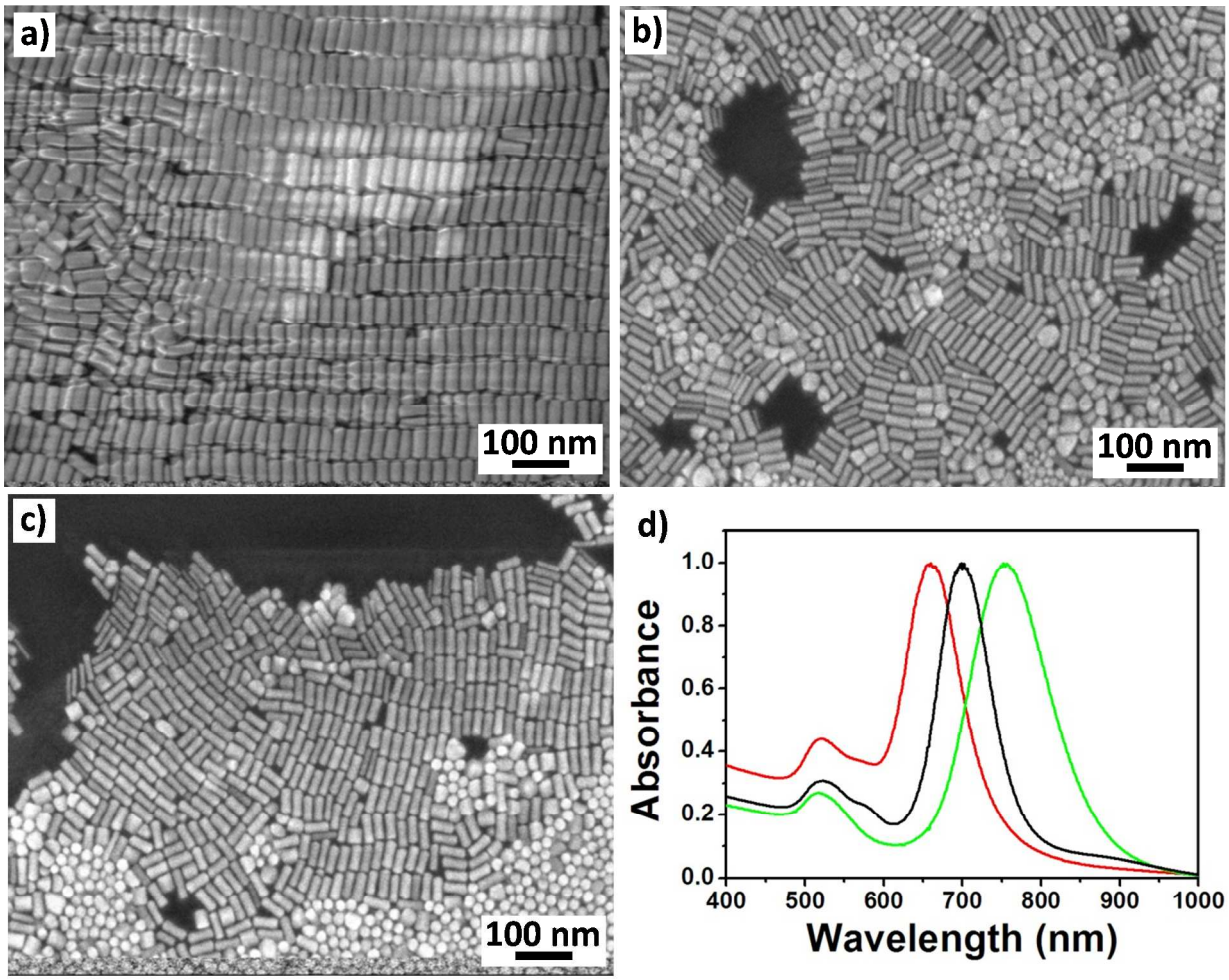


Figure S1. SEM images of synthesized Au nanorods of dimensions: a) 23 × 55 nm, AR = 2.3; b) 19 × 49, AR = 2.6; c) 19 × 60. AR = 3.1; d) UV-vis spectra of synthesized nanorods, red curve nanorods shown in a), black curve nanorods shown in b), green curve nanorods shown in c).

Organic solvent transfer

Au nanorods in water solution were centrifuged and redispersed in water so that the final CTAB concentration was lower than 0.2 mM. Mercapto-succinic acid (3 mL, 10 mM) was added to 3 mL of aqueous nanorod solution. The pH was adjusted to 9 under vigorous stirring. To this solution 1.5 mL of a 50 mM solution of TOAB in chlorobenzene was added. The resulting

mixture was left under vigorous stirring for 30 min until the water phase discolored and the organic phase became intense red.

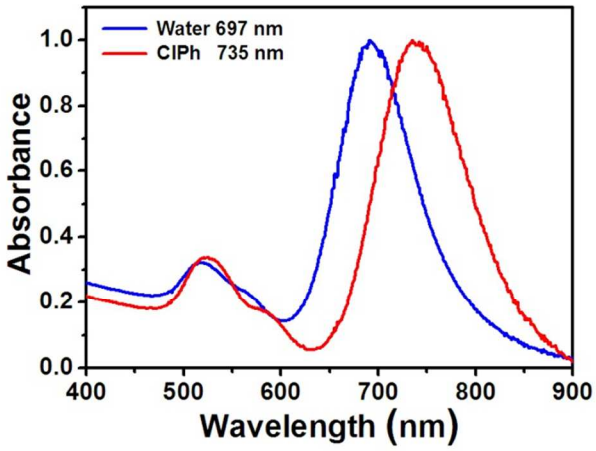


Figure S2. UV-vis spectra of Au nanorods 23 × 55 nm dispersed in water and chlorobenzene.

Influence of nanorod concentration. Self-assembly of Au nanorods 1.4 nM – 14 nM at [CTAB] = 0.1 mM (fast assembly)

Figure S3 shows the influence of nanorod concentration on the formation of vertical superstructures. At low concentration (Figure S3,a) nanorods assembled into spaced domains of average size 2 μm^2. Domain density grew and size increased as nanorod concentration increased from 1.4 nM to 14 nM. The degree of final order and alignment was not influenced by the concentration of nanorods, with low concentration domains forming highly aligned domains (Figure S3,d).

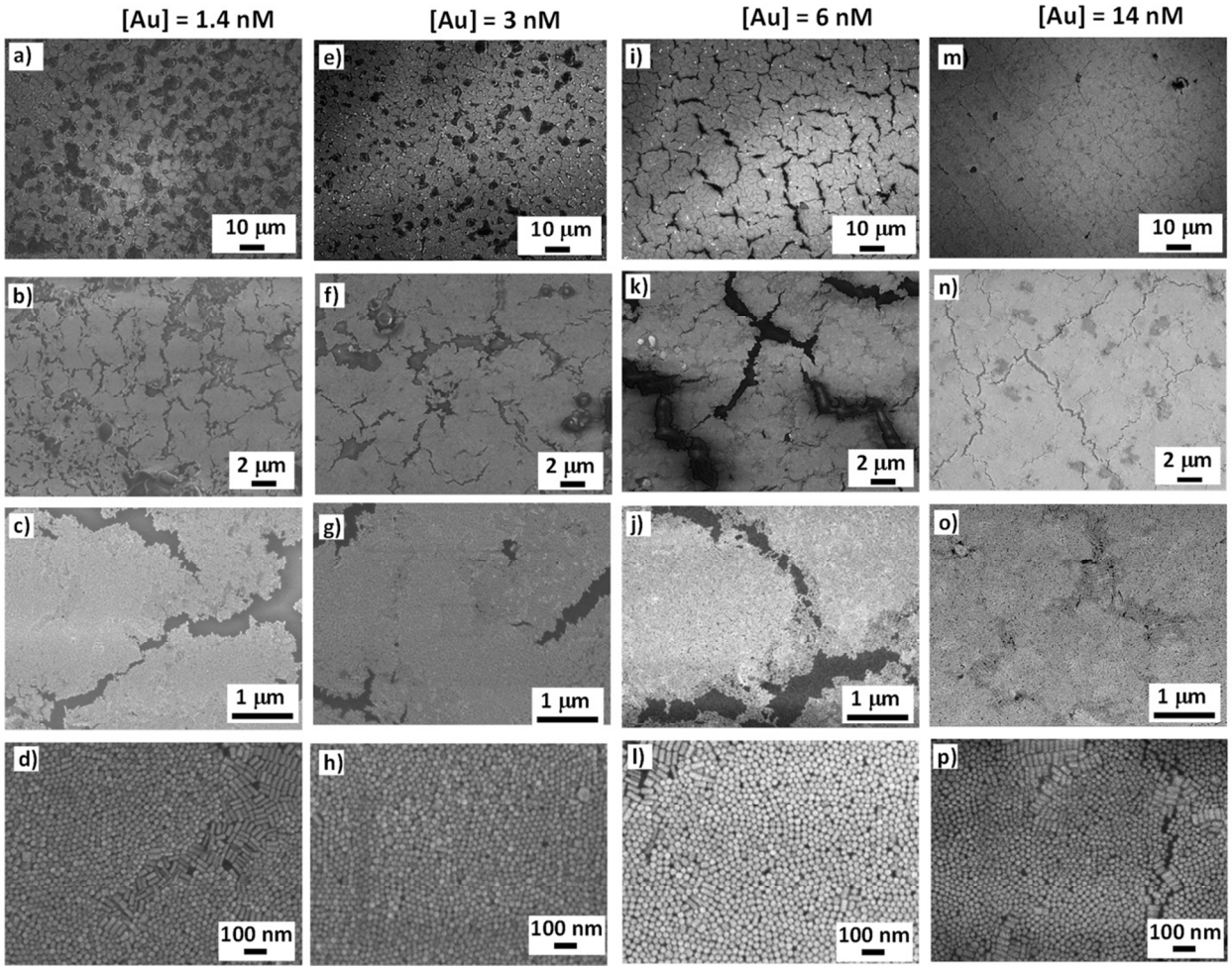


Figure S3. SEM images of nanorod arrays obtained from Au nanorod solutions of 14 nM (a-d); 6 nM (e-h); 3 nM (k-l); 1.4 nM (m-p).

Slow evaporation under Petri dish produced highly dense domains on the periphery of the droplet even at low Au nanorod concentration (Figure S4e). In contrast, the central area was occupied mainly by nanorods lying horizontal to the substrate. The percentage of vertical domains in the central area increased from 16% to 81% as the nanorod solution concentration increased from 1.4 nM to 14 nM.

Calculation of surface coverage

The surface coverage was calculated by image J program using optical images (Figure S5) and was defined as the ratio between the area occupied by the vertical arrays and the sum of the area occupied by horizontal nanorods and empty spaces. Reflection image S4 shows that optical contrast was used to discern between vertically aligned nanorods (gold bright area, circled in blue), nanorods deposited flat on the substrate (dark gold area circled in green) and empty spaces (black areas, circled in red).

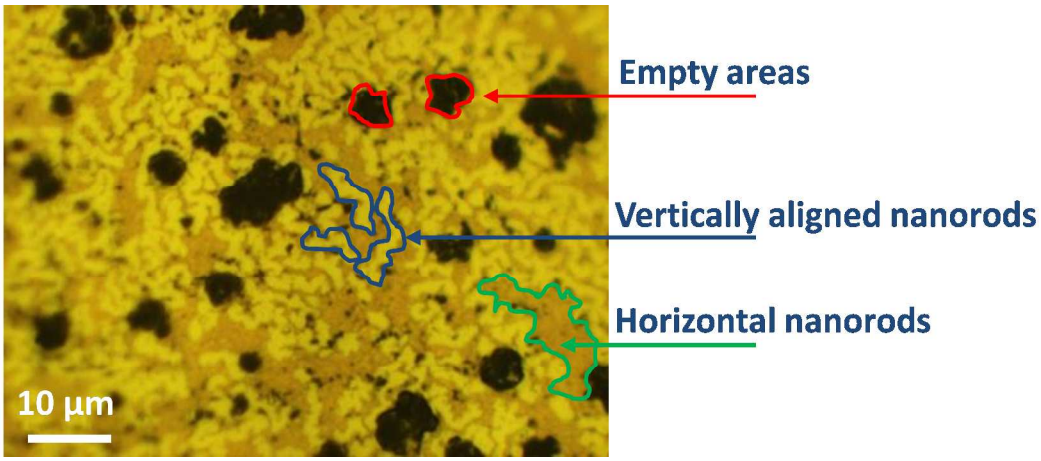


Figure S4. Optical reflection image of nanorod arrays formed by deposition of 10 µL of Au nanorod 1.4 nM on glass coverslips. Blue circles represent areas of vertically aligned nanorods, green circles represent areas of horizontal nanorods, red circles represent empty spaces.

Surface coverage values reported in the manuscript were estimated by image J program from reflection optical images of evaporated droplets of increasing Au concentrations (Figure S5).

Evaporation of the droplet under free air yielded progressively increasing surface coverage (34% to 94%) as the nanorod concentration increased from 1.4 nM to 14 nM.

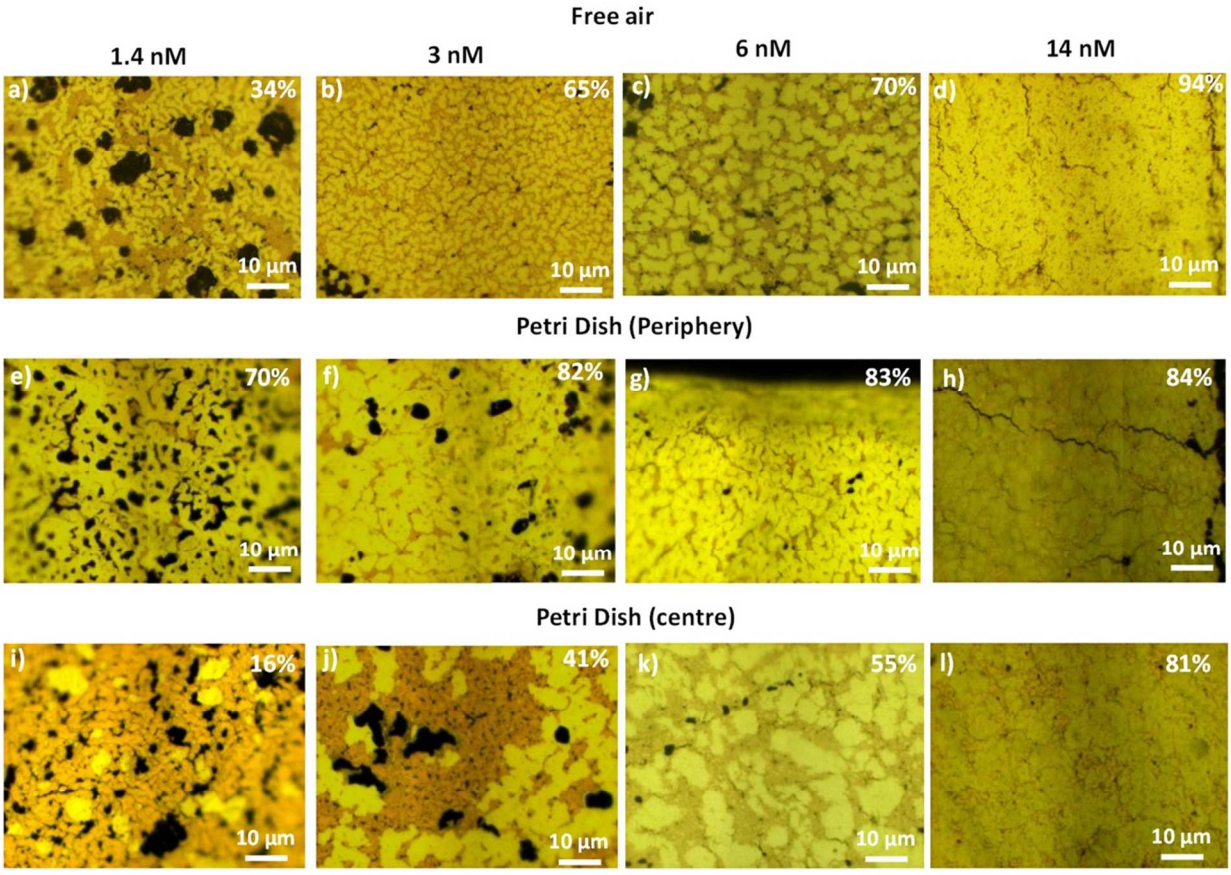


Figure S5. Reflection optical images of nanorod arrays obtained by evaporation of 1.4 nM (a, e, i) , 3 nM (b, f, j), 6 nM (c, g, k) and 14 nM (d, h, l) Au nanorod solutions. Evaporation was conducted in free air (a-d) and under slow conditions (e-l). Coverage percentages reported on the top right corners are calculated by image J program.

Influence of nanorod aspect ratio

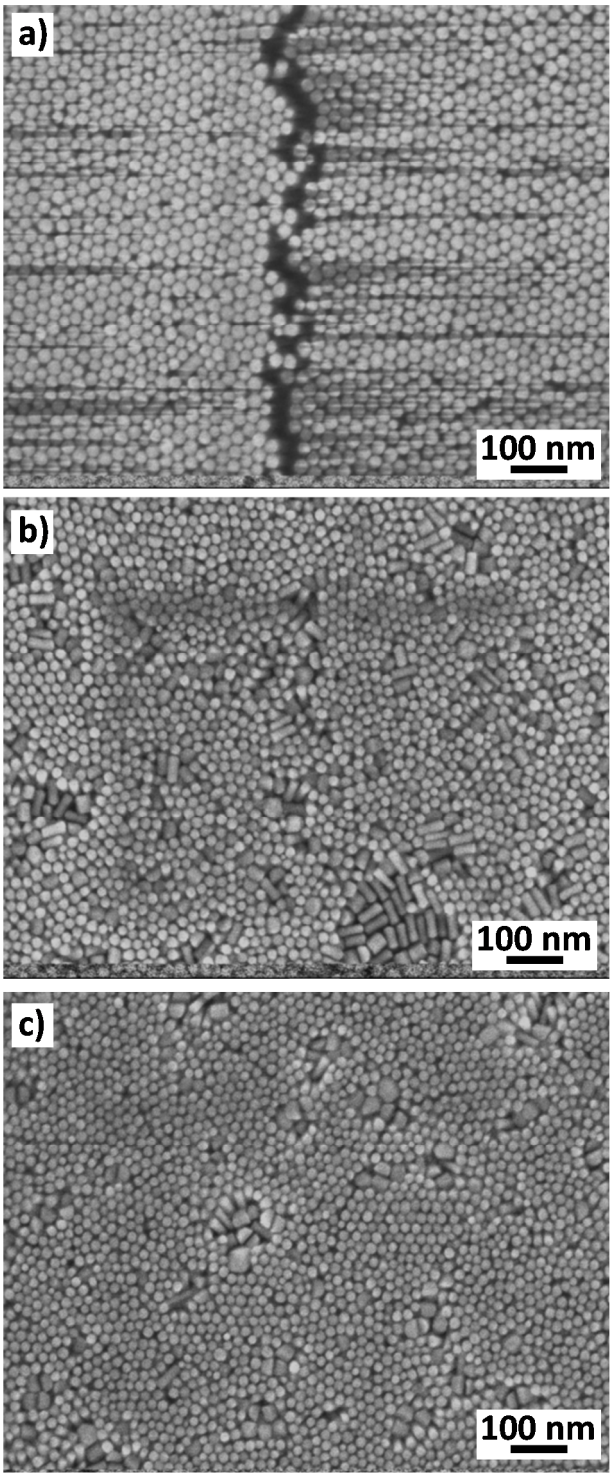


Figure S6. SEM images of vertical arrays formed by droplet deposition of 14 mM Au nanorod solutions with AR 2.3 (a), 2.6 (b) and 3.1 (c).

Self-assembly process was found not dependent from the aspect ratios of deposited nanorods. Figure S6 shows SEM images of ordered arrays formed by nanorods with aspect ratios 2.3, 2.6 and 3.1. Au solution concentration was 14 nM and CTAB concentration 0.1 mM.

Influence of evaporation rate. Self-assembly of Au nanorods 1.4 nM – 14 nM at [CTAB] = 0.1 mM (slow assembly)

Figure S7 shows increasing magnification SEM images of nanorod arrays obtained by deposition of Au nanorod solutions 1.4 nM to 14 nM. The evaporation rate was slowed down to 3 h by application of a petri dish on the evaporating droplet. The images were taken at the periphery of the droplet, where nanorods formed highly aligned domains that grew in size as Au nanorod concentration increased, eventually covering a ring equivalent to ca. 25 % of the entire droplet.

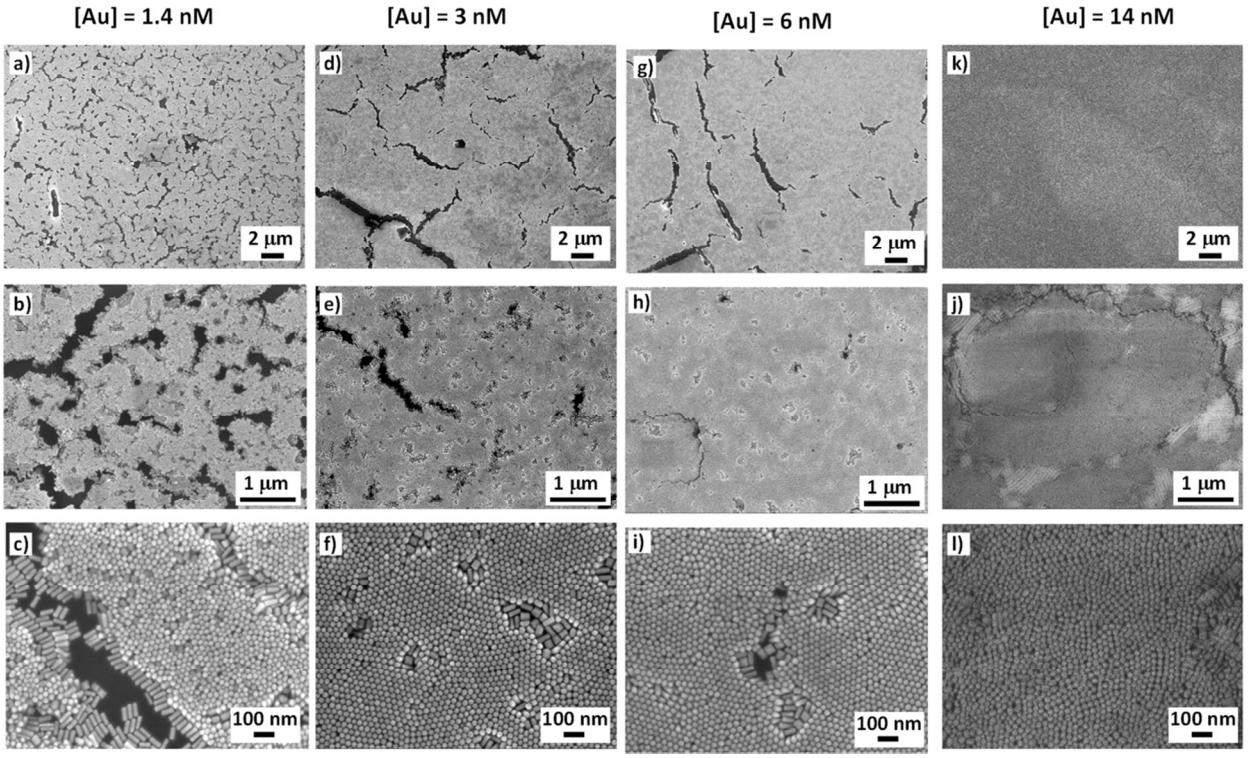


Figure SI7. SEM images of vertical arrays formed by slow evaporation of Au nanorods 1.4 nM (a-c), 3 nM (d-f), 6 nM (g-i) and 1.4 nM (j-l).

Influence of the solvent

The use of chlorobenzene was critical to the formation of ordered arrays. Figure S8 shows SEM images of assemblies obtained by free air evaporation of water solutions (Au concentration 14 nM).

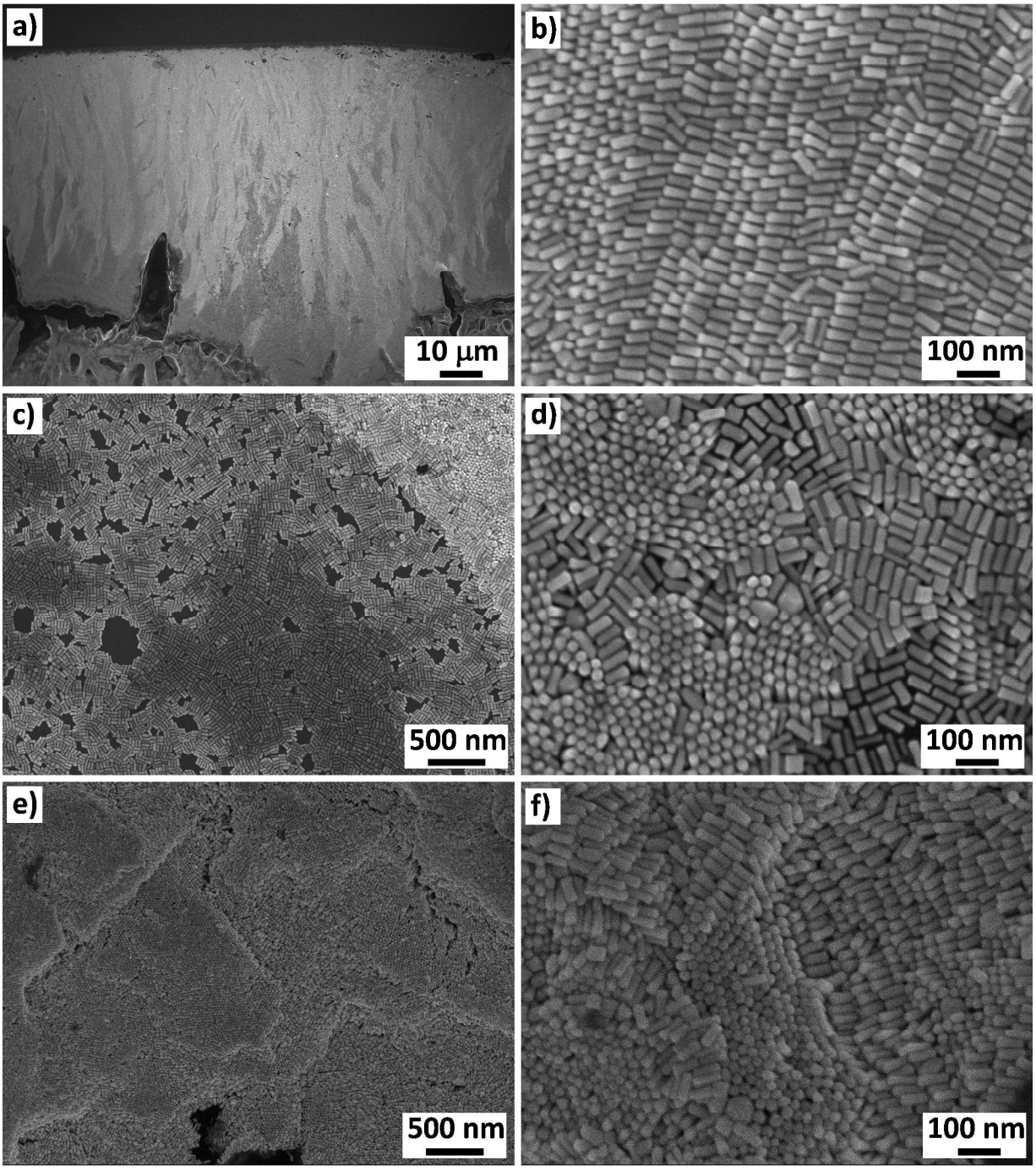


Figure S8. Low (a,c,) and high (b, d,) magnification images of Au nanorod water droplet (14 nM) evaporated under free air.; low (e) and high magnification SEM image of nanorod arrays obtained by fast (20 min) evaporation of water suspensions.

Nanorods accumulated at the periphery of the droplet, according to a coffee stain mechanism (Figure S8a). At the periphery of the droplet multilayered horizontal and vertical nanorod arrangements were found (Figure S8b), whereas in the center of the droplet mainly nanorods lying horizontal to the substrate were observed (Figure S8,d). In order to simulate the time scale of the fast chlorobenzene evaporation (20 min) we also performed fast evaporation of water droplets. Figure S8e,f show low and high magnification SEM images of obtained disordered multilayer arrays.

FDTD simulations of vertical arrays

Figure S9 display the local electromagnetic field enhancement surface plots for vertical arrays with inter-nanorod distance fixed at 2 nm calculated with an incident plane wave along the y direction. The local electric field enhancement factor is defined as $|E/E_0|^2$, where $|E|$ and $|E_0|$ are magnitudes of the local electric field and the incident field, respectively. the cross sectional areas of vertical (x-z plane) and horizontal plane (x-y) were considered, with a plane wave polarized along the x direction. These plots showed that in perpendicular arrays the local fields were highly enhanced along the length of adjacent nanorods.

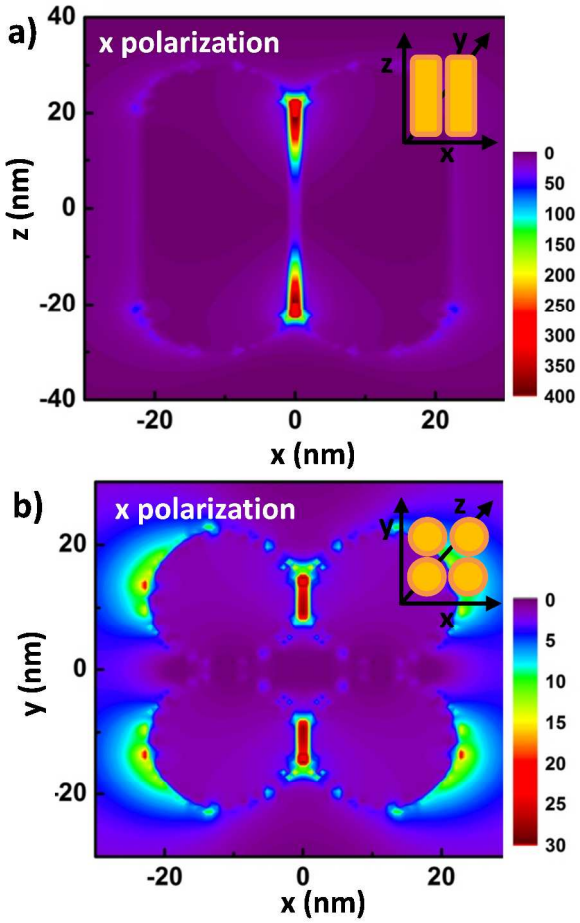


Figure S9. Electromagnetic field enhancement surface plots of nanorod arrays for wave plane incident along the y direction and polarized along the x direction.

MNPBEM Matlab simulations

Figure S10 reports simulated extinction spectrua of a 6×6 nanorod array with inter-nanorod spacing of 1.2 nm -5 nm. The light propagation direction was along the z axis and light was polarized along the x direction (see inset, figure 5 manuscript). The extinction spectra were characterized by broad peaks whose maxima blue shifted as the internanorod distance increased. In particular at internanord 1.2 nm the λ_{max} = 618 nm, at internanord 3 nm λ_{max} = 568 nm, at internanord 4 nm λ_{max} = 552 nm and at internanord 5 nm λ_{max} = 543 nm. Corresponding scattering and absorptipon spectra for increasing internanorod distance are also reported in Figure S10.

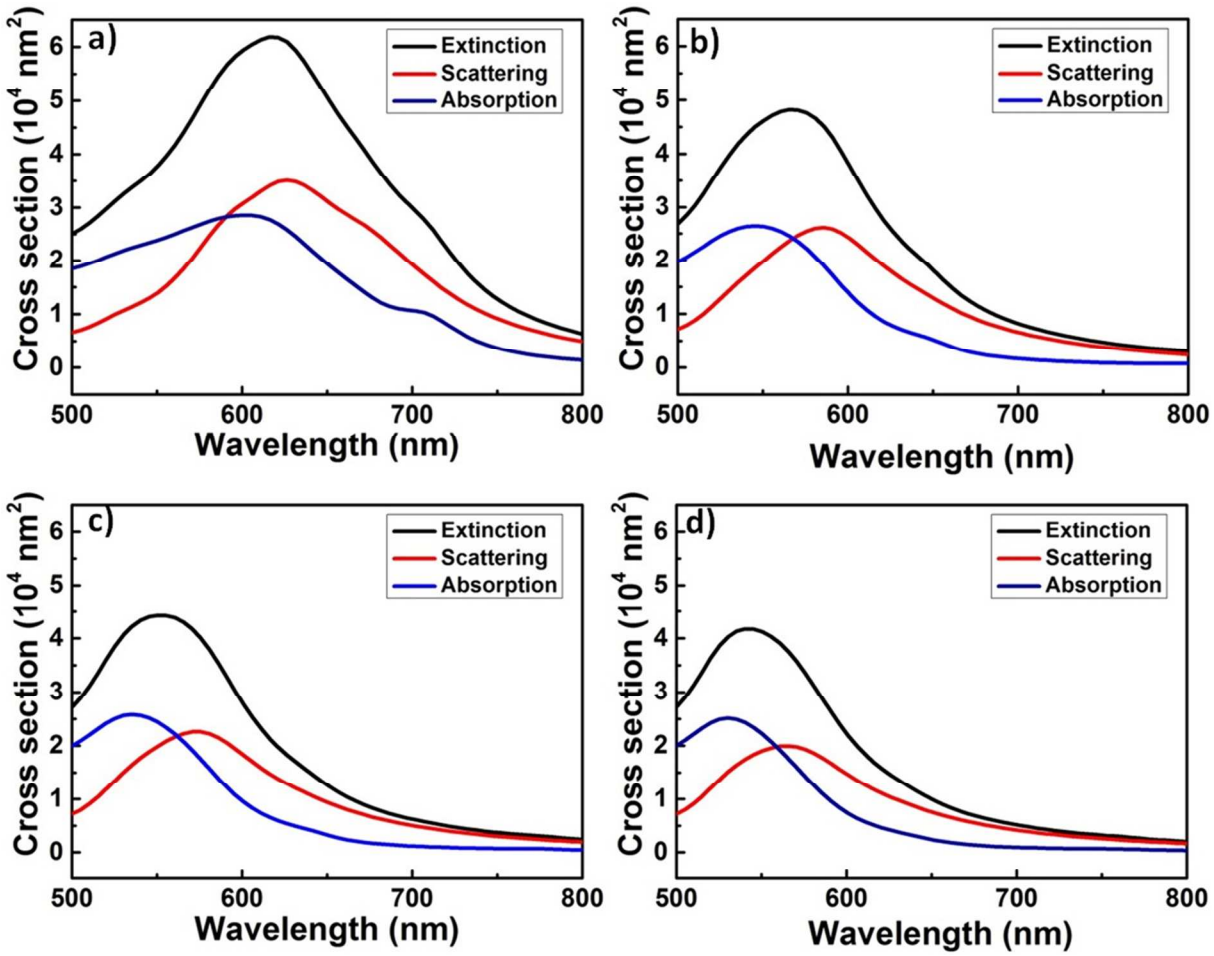


Figure S10. Calculated extinction, scattering and absorption spectra of a vertical 6×6 array with inter-nanorod distance of a) 1.2 nm, b) 3nm, c) 4 nm, d) 5 nm.

Effect of 4-ABT codeposition on vertical assembly formation.

In order to prove that the co-deposition of 4-ABT did not affect the order of formed vertical assemblies, we took SEM images of vertical arrays formed by evaporation of 5 μL 4-ABT solution (1 mM) and 5 μL nanorod solution (14 nM). The SEM images were taken after SERS measurements to confirm that the laser impinging on the sample did not cause any structural damage to the sample.

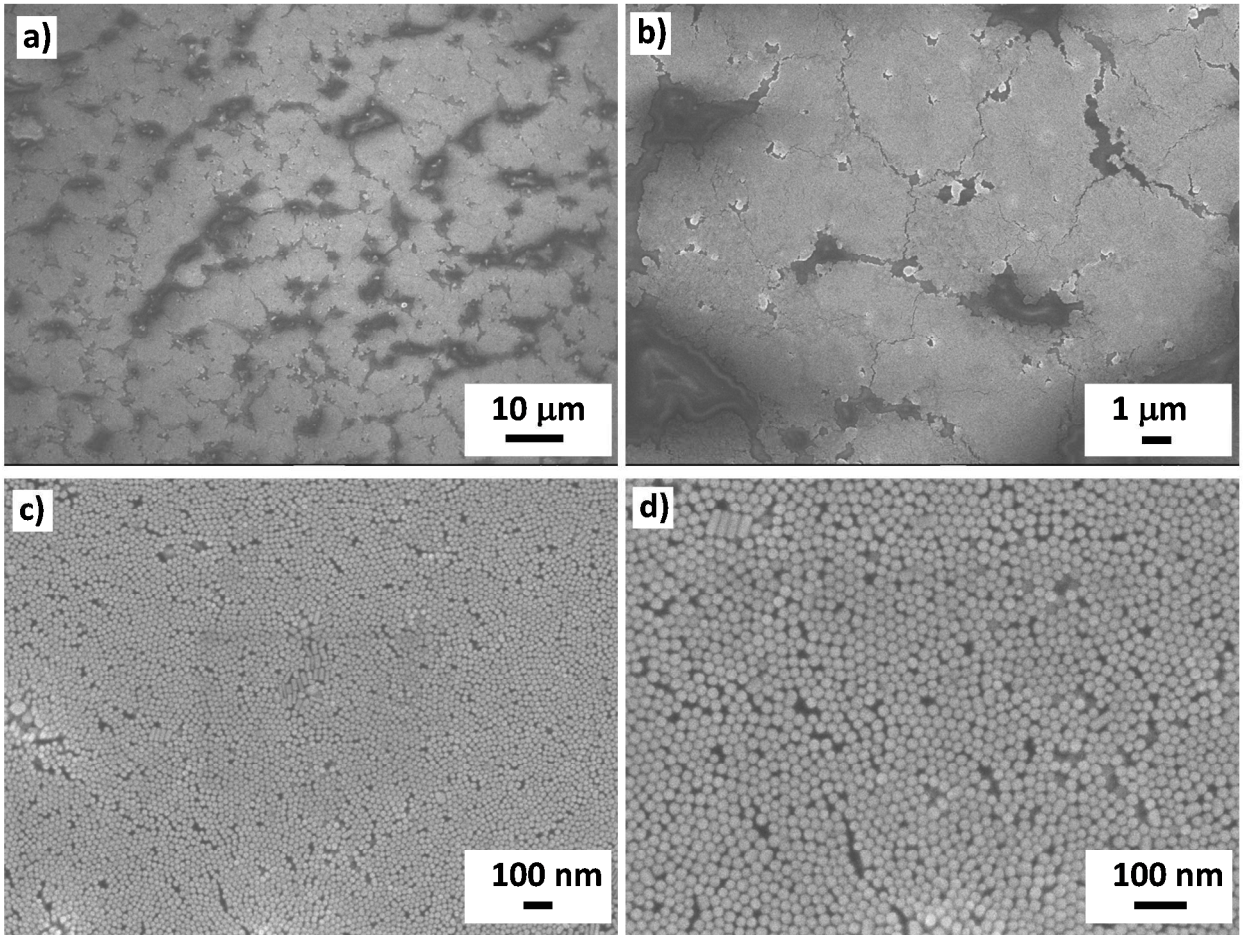


Figure S11. Low to high magnification images of vertical assemblies formed by mixing 5 μL 4-ABT solution 1mM with 5 μL 14 nM Au nanorod solution.