Supporting Information for

Femtosecond Laser-Controlled Tip-to-Tip Assembly and Welding of Gold Nanorods

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CONTENTS

1. MEEP calculations

Optical response and near-field enhancements were calculated using the FDTD method, as implemented in the free software package MEEP.[1] In this method Maxwell equations are solved by a second order approximation. Space is divided into a discrete grid, the Yee grid,[2] and the fields are evolved in time using discrete time steps. A schematic representation of the geometry used for the calculation is shown in Figure S1. Simulations were performed for the polarizations parallel and perpendicular to the structure axis. In all calculations we used spatial resolution of 0.5 nm.
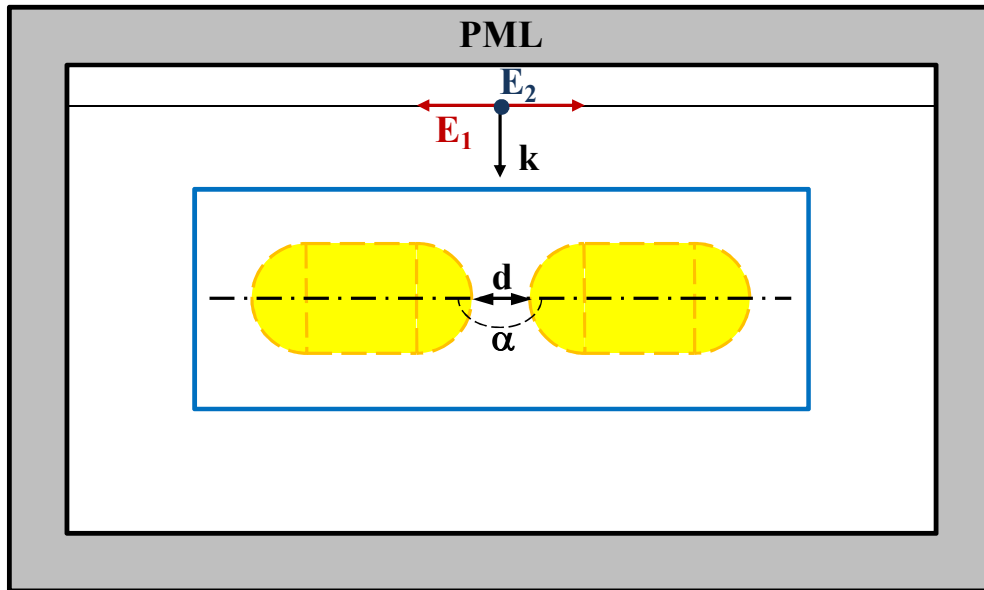

Figure S1. Schematic representation of the geometry used for the FDTD calculations. The dimer structure is surrounded by flux planes (blue lines), in order to calculate the far-field response. Calculations are performed for light polarized parallel (red) and perpendicular (dark blue) to the structure axis. The entire cell is surrounded by a perfectly matched layer, in order to simulate an infinitum space.

2. Characterization techniques

***Transmission electron microscopy*:** TEM images were obtained with a JEOL JEM-1400PLUS transmission electron microscope, operating at an acceleration voltage of 120 kV. High Resolution TEM images were recorded using a JEOL2010F FE-TEM instrument operating at 200 kV. Carbon-coated 400 square mesh copper grids were used. All the samples were centrifuged at least once before blotting on the grid.

High resolution high angle annular dark field scanning transmission electron microscopy: HAADF-STEM images were acquired using a double aberration corrected Titan 50-80 microscope operating at 300 kV in STEM mode.

***UV/Vis/NIR measurements*:** UV/Vis/NIR absorption spectra were registered using a Cary 5000 UV-Vis-NIR. All experiments were carried out at 298 K, using quartz cuvettes with optical paths of 0.1 cm.

In situ UV/Vis measurements: A schematic representation of the *in situ* experimental setup is shown in Figure S2. Samples were illuminated with a halogen lamp that was directed by a silica optical fiber of 200 μm diameter and converted to a nearly-parallel beam using silica lens. Transmitted beam was collected and focused with a similar silica lens into a silica optical fiber of 1 mm diameter. The light was guided to a compact spectrometer, QE6500 (Ocean Optics Inc.), configured with a multichannel array detector for measuring simultaneously the whole spectrum in the range 400-1000 nm with a spectral resolution better than 2 nm. The reflectance spectra were recorded using an integration time of 1 s.
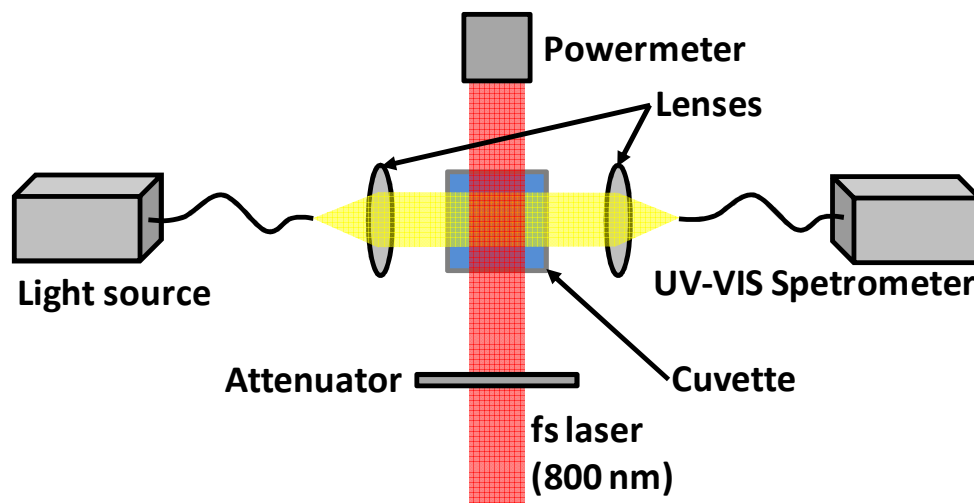
Figure S2. Schematic of laser irradiation setup used to monitor the assembly kinetics of AuNRs in real time. A linearly polarized 800 nm pulsed laser (50 fs) is passed through a quartz cuvette such that it fully illuminates the solution containing the nanoparticles. Its power is adjusted with a variable attenuator wheel. Variations in the relative concentration of the AuNR assembled species are monitored based on the extinction of the light of a halogen lamp, which is passed through the cuvette in a perpendicular direction.

3. Synthesis, capping agent replacement and assembly of AuNRs

Materials: All the starting materials were obtained from commercial suppliers and used without further purification: Hexadecyltrimethylammonium bromide (CTAB, ≥99%), 5-bromosalicylic acid (technical grade, 90%), hydrogen tetrachloroaurate trihydrate (HAuCl$_4$·H$_2$O, ≥99.9%), silver nitrate (AgNO$_3$, ≥99.0%), L-ascorbic acid (≥99%), sodium borohydride (NaBH$_4$, 99%), branched polyethylenimine of average molecular weight of 25kDa (PEI), ammonium hydroxide solution **(**28.0-30.0% NH$_3$), 1,8-octanedithiol(HS(CH$_2$)$_8$SH), acetic anhydric

(≥98.0%) and ethanol (96%) were purchased from Aldrich. Nanopure water (resistivity 18.2 MΩ·cm at 25 °C) was used in all experiments.

Synthesis and overgrowth of Au NR*:* The seeds were prepared by the standard CTAB/NaBH$_4$ procedure: 25 µL of a 0.05 M HAuCl$_4$ solution was added to 4.7 mL of 0.1 M CTAB solution; 300 µL of a freshly prepared 0.01 M NaBH$_4$ solution was then injected under vigorous stirring. Excess borohydride was consumed by keeping the seed solution for 30 min at room temperature prior to use. Gold nanorods were prepared, with some modifications, as previously described by Scarabelli[3]. In a typical synthesis of a 50 mL NR solution, 45 mg of 5-bromosalicylic acid was added to 50 mL of 0.05 M CTAB. The solution was mildly stirred for 15 min until complete dissolution, and 480 µL of 0.01 M AgNO$_3$ and 500 µL of 0.05 M HAuCl$_4$ solution was added to the mixture. After 2 h at 25°C, 130 µL of 0.1 M Ascorbic acid solution was added under vigorous stirring, followed by 80 µL of seed solution. The mixture was left undisturbed at room temperature for at least 4 h. The resulting gold nanorods presented a LSRP with an absorption maximum at 660 nm. (Figure S3).Typically, 50 mL of the mixture was centrifuge (6000 rpm, 30 min) and the precipitate was redispersed in the same volume of a solution of 0.05 M CTAB, containing 45 mg of 5-bromosalicylic acid, 700 µL of 0.01 M AgNO$_3$, 500 µL of 0.05 M HAuCl$_4$ and 250 µL of ascorbic acid. The solution was slowly heated to 90°C in a water bath, and maintained until the LSRP of the NR blue shifted to 600 nm. At this point, the mixture was rapidly cooled down and NRs were washed by centrifugation (6000 rpm, 30 min). Finally, they were redispersed in 10 mL of 2 mM CTAB solution. The resulting CTAB-stabilized AuNRs (CTAB-AuNRs) presented a length and diameter of 58 ± 4 nm and 34 ± 4 nm, respectively, and an aspect ratio of 1.7, as determined from TEM images (Figure S3).
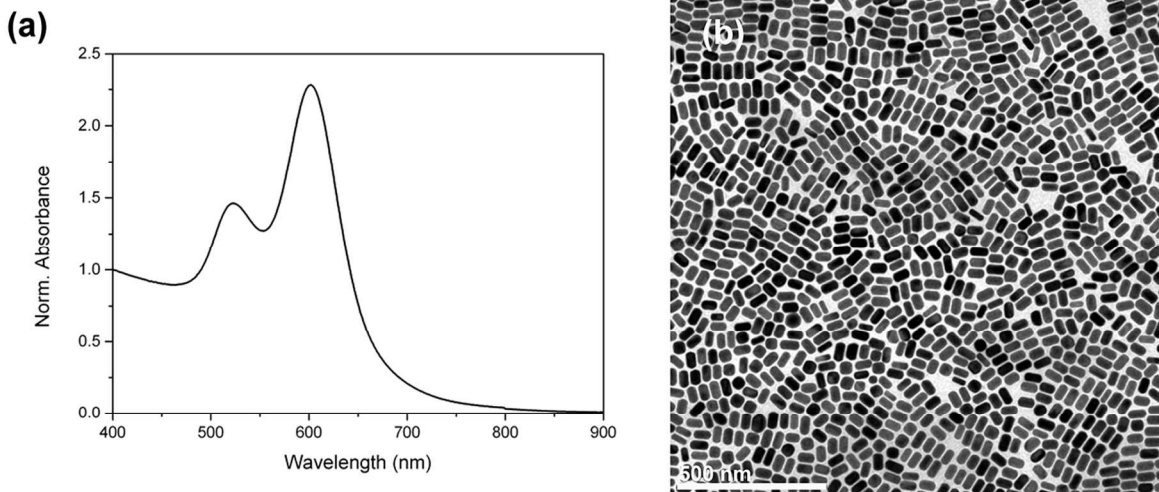
Figure S3. (a) Extinction spectra and (b) representative TEM image of synthesized CTAB-AuNRs in water.

4. Capping polymer replacement and assembly of AuNRs

Materials: All the starting materials were obtained from commercial suppliers and used without further purification: branched polyethylenimine of average molecular weight of 25kDa (PEI), ammonium hydroxide solution (28.0-30.0% NH_3), 1,8-octanedithiol($HS(CH_2)_8SH$), acetic anhydric (≥98.0%) and ethanol (96%) were purchased from Aldrich. Nanopure water (resistivity 18.2 MΩ·cm at 25°C) was used in all experiments.

Capping polymer replacement: Typically, 1mL of 100 mg/mL aqueous solution of PEI, previously sonicated for 5 minutes, was added drop wise to 4 mL of a CTAB-AuNRs solution (2 mM CTAB, 5 mM Au) under stirring. The solution was kept undisturbed for at least 2h. After the reaction time, the excess of free PEI was removed from the solution by one centrifugation cycle (3300 rpm, 30 minutes). The precipitate was redispersed in ethanol, adjusting the concentration of gold to 30 mM. (Figure S4).
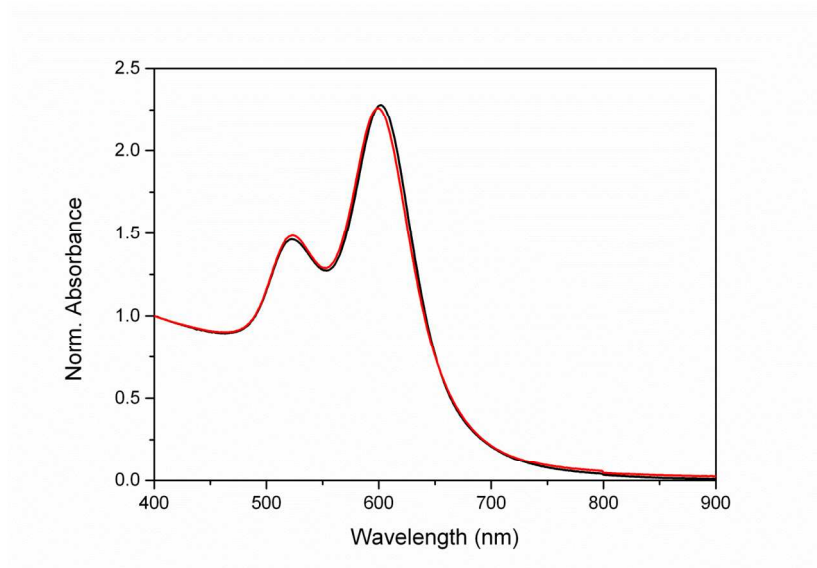
7

Figure S4. Extinction spectra of CTAB capped AuNRs in water (Black) and PEI capped AuNRs in ethanol (Red).

Assembly of AuNRs:

- *Initiation of the polymerization:* 150 μL of ethanol solution of PEI-AuNRs were mixed with 150 μL of 1,8 octanedithiol (0.5 mM to 0.1 mM, depending on the desired rate of polymerization) ethanolic solution containing also 0.02% v/v of ammonium hydroxide solution (Figure S5)

- *Termination:* Termination was achieved at any stage of the polymerization by addition of 40 μL of anhydric acetic and 40 μL of 25 mg/mL of maleimide ethanol solution the reaction mixture (Figure S6).
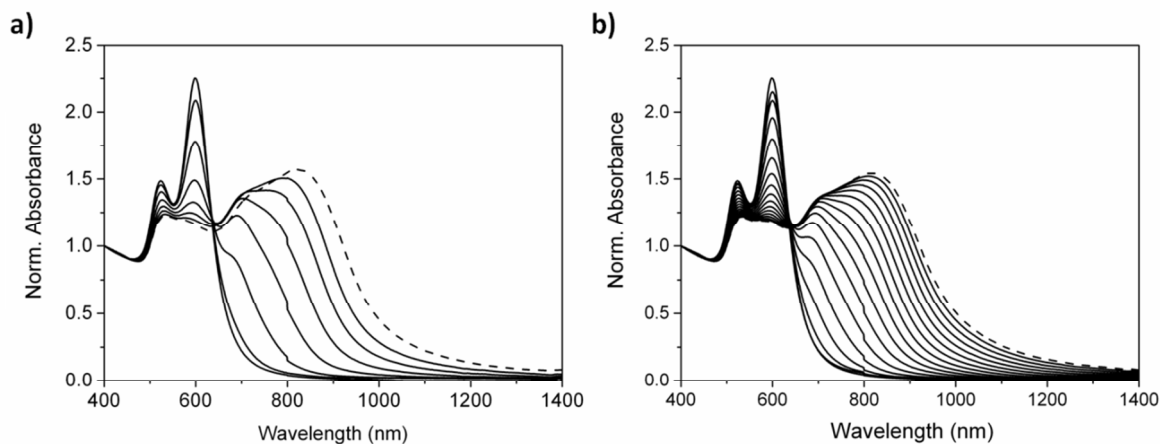
Figure S5. (a) Extinction spectra of AuNRs polymerization in ethanol in the presence 1,8-octanedithiol at 0.25 mM (a) and 0.05 mM (b), acquired at time intervals of 90 sec.
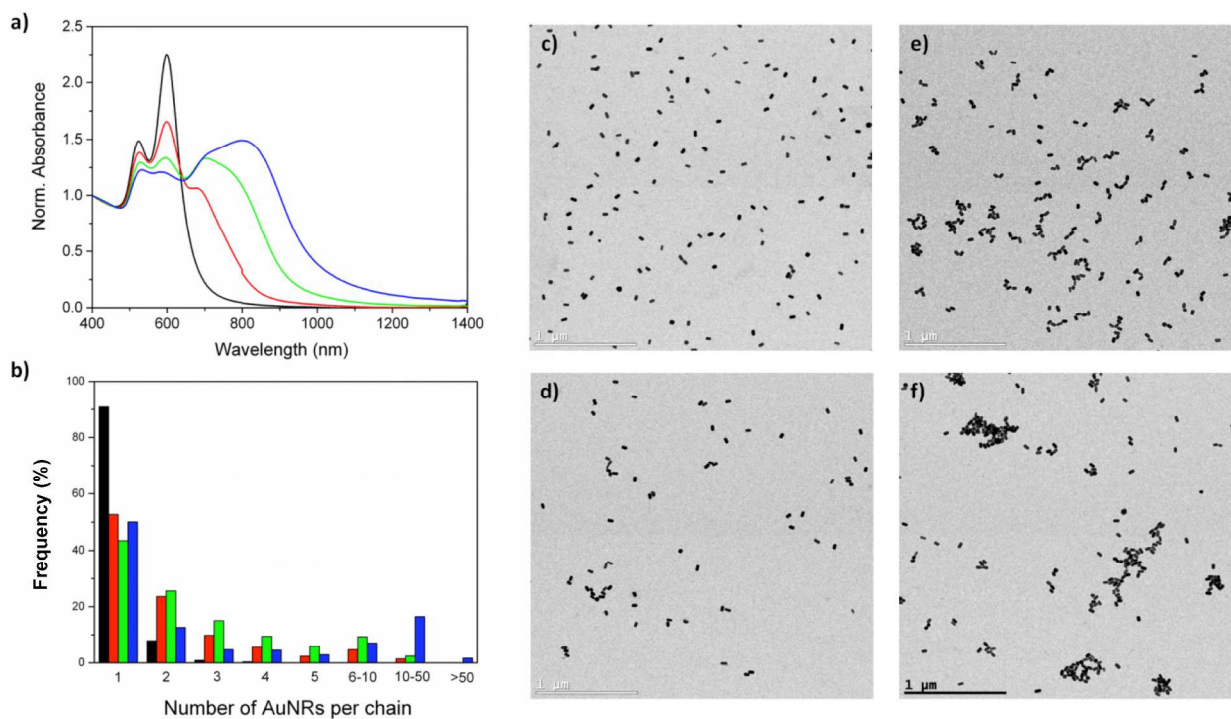

Figure S6. (a) Extinction spectra during AuNRs (~10^9 M) assembly in ethanol, using 1,8-octanedithiol (0.5 mM) as linker, stopped with maleimide (0.25 mM) at different times: 0 (black curve), 4.5 (red curve), 8 (green curve) and 12 (blue curve) minutes, (b) their population

distribution for 0 (black bars), 4.5 (red bars), 8 (green bars) and 12 (blue bars) minutes and, (c-f) some representative TEM micrographs for each selected time.

5. Femtosecond laser control of the assembly.

Equipment: 50 fs laser pulses were generated by an amplified Ti-Sapphire amplified laser system (Spectra Physics) centered at 804 nm operating at a repetition rate of 1 kHz. The temporal profile of the 804 nm pulses was diagnosed by second harmonic autocorrelation whereas fluence control was performed by a variable attenuator wheel. A mobile mirror was used to scan the cuvette with the laser beam in order to ensure a proper irradiation of the entire volume.

6. Calculating the concentration of the species.

In situ measurements of the extinction spectra were used to study the evolutions of the relative concentration of the main species. Then, experimental spectra were fitted with a weighted average of the theoretical spectra calculated using FDTD (shown in Figure 1a), in order to obtain the relative concentration of the main species. Possible configurations for the AuNRs oligomers are rather large, far more than can be simulated, which introduces an error in the concentrations yielded by our model. Based on the TEM analysis we have assumed that the AuNRs are bonded preferentially by the tips, which considerably reduces the number of possible configurations. Moreover, as we have discussed in the main text, the angle between the AuNRs does not change the position of the LSPR but only its intensity. The only configuration without tip-to-tip links that we found in appreciable quantities by TEM was the side-by-side dimer and, consequently, we also included their extinction spectra in the fit. Additionally, we considered the spectra for the main species (single AuNRs, dimers and trimers), whereas all larger-chain oligomers were approximated by a Gaussian curve. In spite of its simplicity, the model is able to yield reasonable

results for the relative concentrations of the main species. Some representative fits (for the unirradiated sample) are shown in Figure S7, as can be seen there, the fits are very good. Then, we repeat this fitting for every step of the reaction and can obtain the curves depicted in Figure 5d-f of the main text.
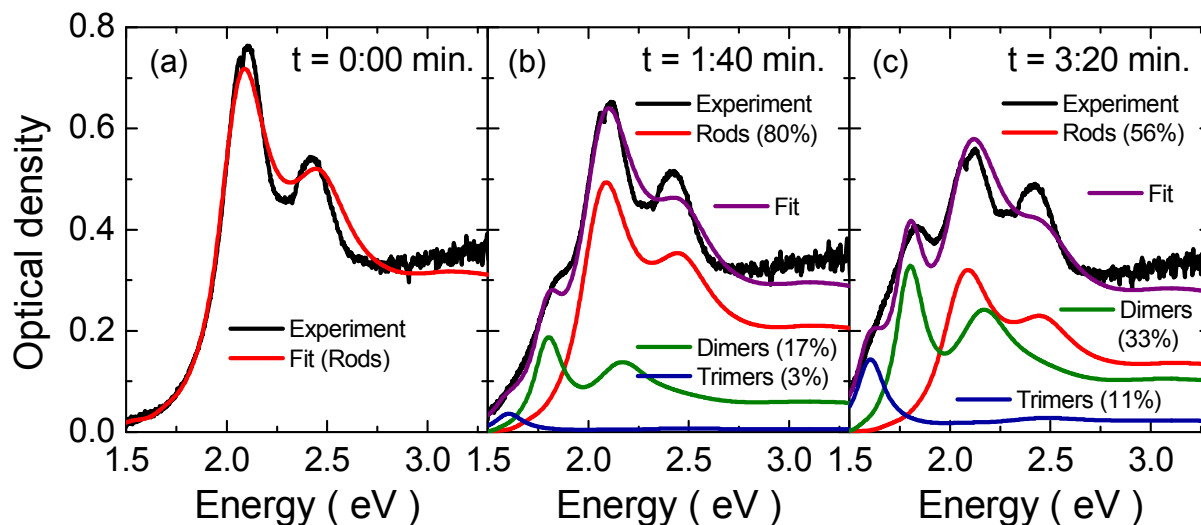

Figure S7. Extinction spectra measured for different stages of the polymerization reaction in the non-irradiated solution (black lines). Best fits and the corresponding concentrations of the main species are also shown.

7. References

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