

Driving Chemical Reactions in Plasmonic Nanogaps with Electrohydrodynamic Flow

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Supplemental Information

Au nanospheres were assembled on PS-b-PMMA diblock copolymer templates on a Cu TEM grid without an applied bias to examine gap spacings between nanospheres in the absence of electrohydrodynamic flow. Figure S1a depicts a TEM micrograph of 40 nm radius Au nanospheres assembled on the copolymer coated copper TEM grid. The gap spacing of the dimer observed in Figure S1 is approximately 3.6 nm. Without EHD flow, gap spacings are not controlled by anhydride crosslinking, leading to a high degree of variability in observed values. Figure S1b depicts a SERS spectra acquired from a Control substrate assembled as described in the main text. Control substrates are sparsely populated with oligomers and have increased gap spacings with respect to EHD substrates. Thus higher laser excitation intensities are necessary to collect SERS spectra with similar intensity as the EHD substrates; here 7.3 mW laser power is used compared to the 73 μ W used for EHD substrates. No significant peaks are observed that correspond to the anhydride vibrational modes identified in the main text and highlighted with a dashed line in Figure S1b. The scattered intensity near 1600 cm^{-1} is associated with carboxylate vibrational modes from the lipoic acid.

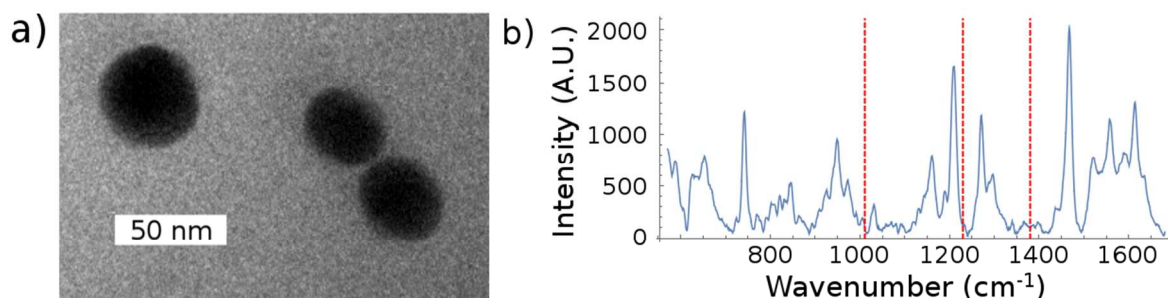


Figure S1: (a) TEM micrograph of an assembled oligomer without an applied bias Control substrate. (b) Surface enhanced Raman scattering (SERS) spectra from a similar Control substrate acquired at 785 nm with a laser power of 7.3 mW for 1s. Dashed red lines indicate spectral positions associated with anhydride linked samples.

To analyze the degree of oligomerization of a given oligomer and the number of nearest neighbors of a given Au nanoparticle, Wolfram MathematicaTM is implemented for image analysis. SEM images, an example shown in Figure S2 a, are first binarized, and oligomers are distinguished from one another as being separate collections of foreground pixels, or morphological components. Single Au nanoparticle are identified through their circularity, defined as the ratio between the equivalent disk perimeter length and the perimeter length of a polygon formed by the centers of each perimeter element, only morphological components over a certain threshold of circularity are determined to be single nanoparticles. The remaining morphological components are then divided into component nanoparticles using a modified Euclidean distance transform approach, which is designed for implementation in SEM images, where edge effects can make identification of small nanoparticles in close packed structures difficult. For each morphological component, the original image is again binarized using local adaptive binarization, shown in the left side of Figure S2 (b). A Euclidean distance transform (figure distance transform) then reveals the nanoparticle centers as local maxima, shown in the right side of Figure S2 (b). The maxima are then used to determine the center of each nanoparticle and a distance threshold is used to determine the number of nearest neighbors of a given nanoparticle. From these images the number, density, and nearest neighbor statistics are obtained as shown in Figure S2 (c) and (d), respectively.

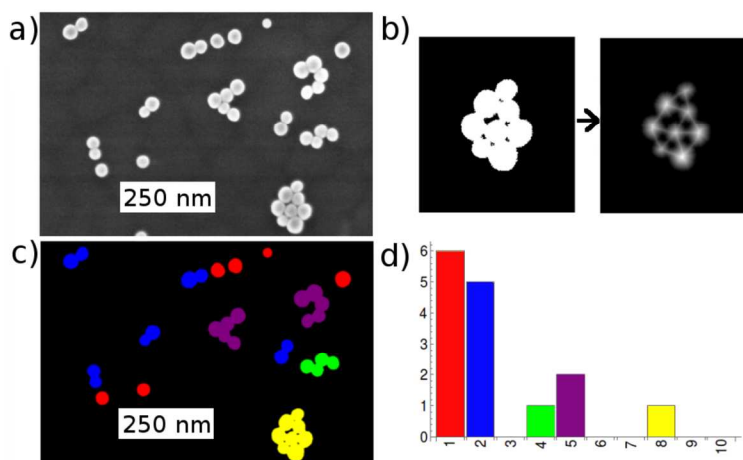


Figure S2 (a) SEM image of 40 nm EHD-anhydride substrate (b) left: local adaptive binarized oligomer, right: distance transform of the left image (c) Colorized image of the SEM image with oligomers identified (d) Histogram of the number oligomers identified for each degree of oligomerization.

Figure S3 depicts a TEM micrograph of a dimer assembled on a 20 nm EHD-anhydride substrate. The pictured substrate was assembled at room temperature. The gap spacing is consistent with anhydride linking, indicating that EHD flow induced anhydride crosslinking still occurs with particles as small as 20 nm.

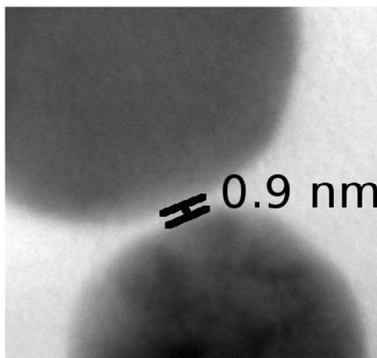


Figure S3: TEM micrograph of a dimer assembled on a 20 nm EHD-anhydride substrate.

Multiple deposition steps may be used to increase the degree of oligomerization on a sample. Figure S4 depicts an SEM image of a 60 °C EHD substrate after four deposition steps, leading to greater oligomer density than the two deposition step samples presented in the main text. Here, we begin to see the formation of three dimensional oligomers as electrophoresis drives Au nanospheres onto existing oligomers.

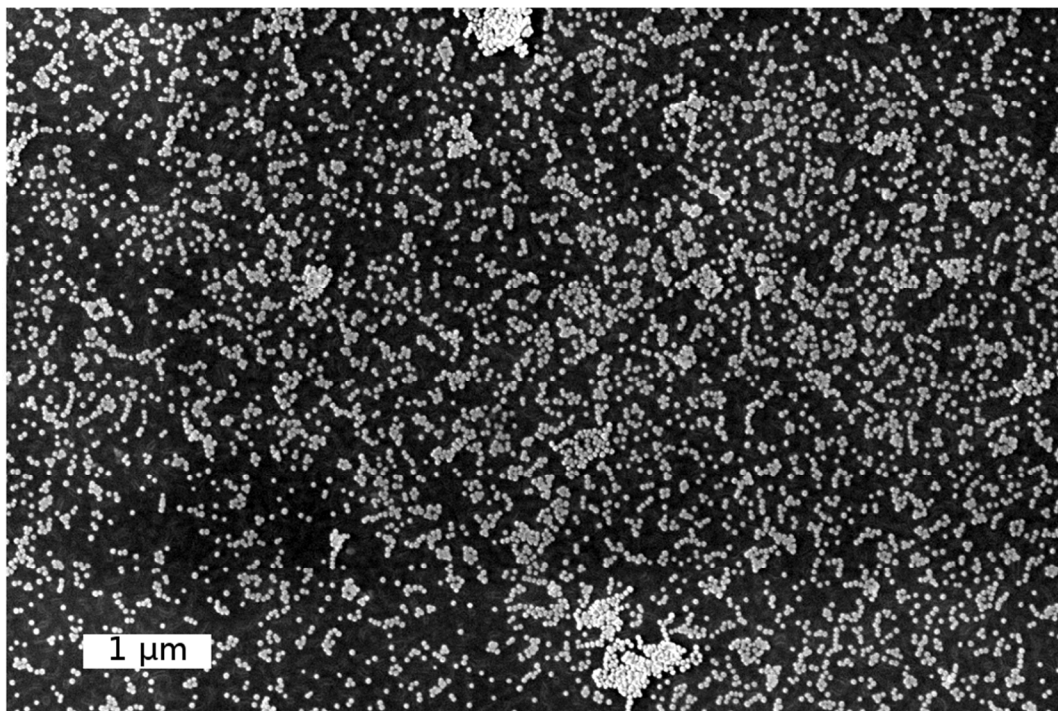


Figure S4: SEM image acquired from a 60 °C EHD substrate after four depositions with 35 μ L EDC and s-NHS solution in each deposition.

Figure S5 depicts oligomers on a 60 °C EHD substrate with the underlying block copolymer template visible in the imaging conditions. Au nanospheres within the oligomers are observed on the amine-functionalized PMMA domains (dark with bright borders) and on PS regions. Anhydride crosslinking of Au nanospheres to one another, where one or more of the nanospheres in the oligomer is bound to the PMMA domain or PS/PMMA domain boundary, will result in some nanospheres on the PS region. PMMA domains appear darker with bright edges due to topography changes during the ethylenediamine functionalization step; see Ref. 10 in main text. Thus they can be observed in SEM images when using lower current and accelerating voltage.

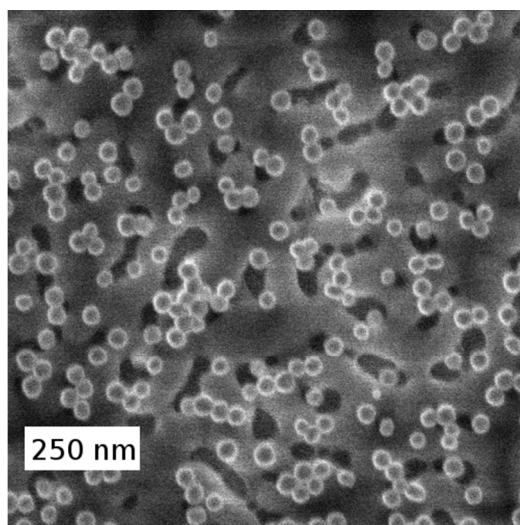


Figure S5: SEM image acquired at 2 KeV and 13 pA from a 60 °C EHD substrate to highlight the PS-b-PMMA block copolymer template.

Additional SERS data is also provided here to further demonstrate reproducibility and stability of SERS response from EHD anhydride substrates. Figure S6 includes SERS spectra acquired from samples undergoing the same treatments discussed in the main body text in Figure 2b,c. The five different spectra in each panel come from 5 different samples. Reproducible SERS signal is observed for the (a) anhydride, (b) methylamine, (c) aniline and (d) benzenethiol. SERS signal after treatment of (b) methylamine has peaks associated with carbonate groups in lipoic acid in the region around 1600 cm^{-1} . The data is slightly noisier and is consistent with less ordered molecular orientations in the hotspot. Figure S7 depicts SERS spectra before (lower) and after (upper) soaking samples in DI water for 7 days after undergoing treatments discussed in the main body text in Figure 2b,c. No additional treatment is performed after the 7 day soak. The similarity of spectra observed after soaking the samples demonstrates that the Au nanosphere oligomers are stable in aqueous solution.

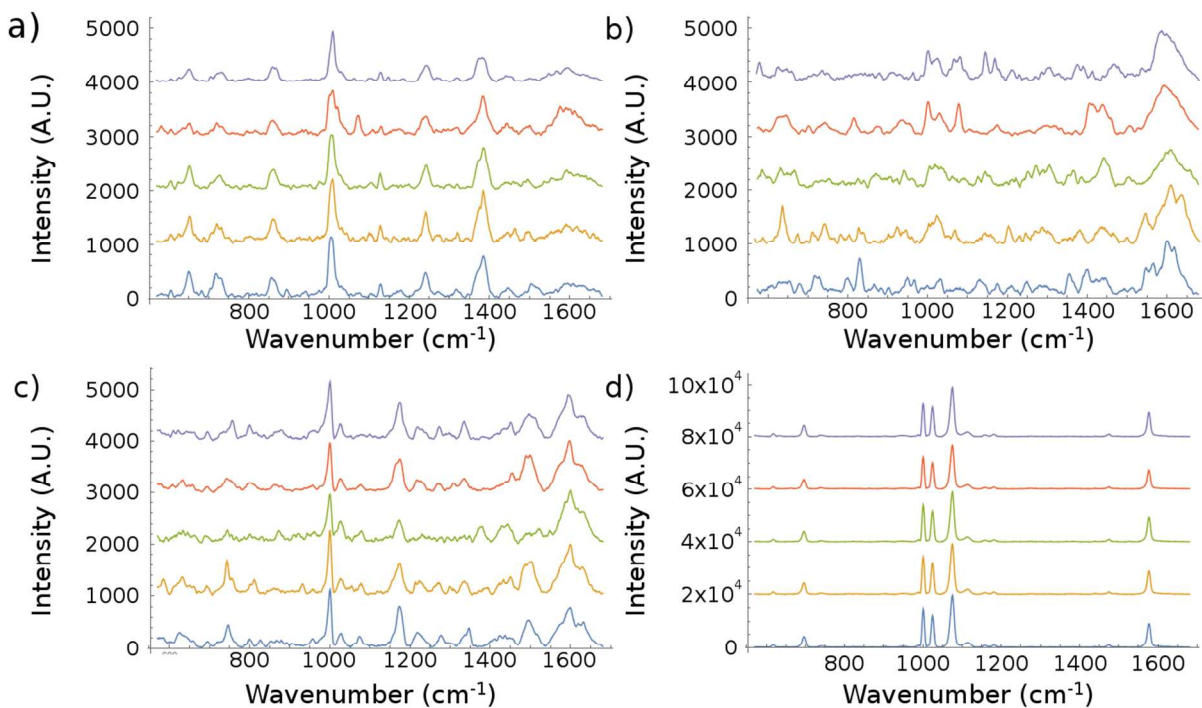


Figure S6 SERS spectra acquired from 5 different EHD-anhydride samples in the following conditions: a) untreated sample b) methylamine treated sample c) Aniline treated sample d) plasma cleaned benzenethiol treated sample.

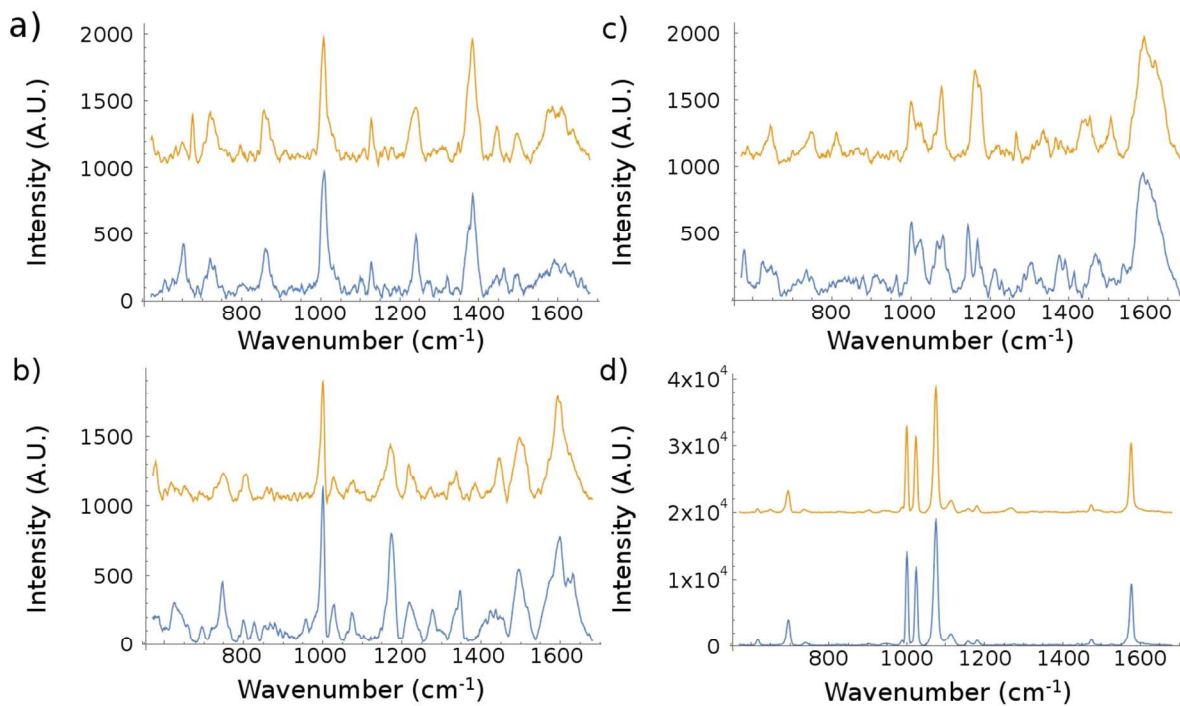


Figure S7 SERS spectra acquired from: an a) untreated sample, b) methylamine treated sample, c) aniline treated sample, and d) plasma cleaned benzenethiol treated sample before (lower curve) and after (upper curve) soaking the sample in DI water for 7 days.