Supplementary Information

Materials:

Hydrogen tetrachloroaurate (III) hydrate ($HAuCl_4 \cdot 3H_2O$), sodium dodecyl sulfate (SDS), tris (2-carboxyethyl) phosphine hydrochloride (TCEP), silver nitrate ($AgNO_3$), sodium borohydride ($NaBH_4$), L-ascorbic acid, trisodium citrate dihydrate (SC), citric acid (CA) were purchased from Sigma-Aldrich. mPEG-thiol is purchased from Polypure. All chemicals were used as received without further purification. All chemical synthesized DNA strands were purchased from Integrated DNA Technologies, Inc. (www. Idtdna.com). The unmodified helper strands were ordered in a 96-well plate format, suspended in ultrapure water without purification. All modified strands were ordered from IDT with PAGE purification. 100kDa MWCO centrifuge filters were purchased from Pall, Inc.

Experimental Methods:

Self-assembly of DNA origami rectangle

A DNA origami template was formed according to the Rohtermund method (reference S1). M13 viral DNA and all of the staple strands were mixed together at a 1:5 ratio, in a 1 x TAE buffer solution containing 40 m of M Tris-HCl, 20 mM of acetic acid, 2 mM of EDTA, and 12.5 mM of magnesium acetate. The DNA origami solution was slowly cooled from 90 °C to 16 °C with PCR for over 3 hours. The final concentration of M13mp18 DNA genome in the solution was 20 nM. DNA origami was then purified to remove the excess DNA helper strands using 100kDa MWCO centrifuge filters. The formation of DNA origami/GNPs assemblies was annealed from 45 degree to room temperature in a 2-liter water bath stored in a styrofoam box over the course of 18 hours.

Synthesis of gold nanoparticles

The detailed procedure can be found in reference S2 with slight modification. Briefly, 15nm GNPs were synthesized by using SC (trisodium citrate dihydrate) to reduce $HAuCl_4$. 160 µl of 50mM $HAuCl_4$ were added to 50 ml of nanopure water and heated to boiling. Then 2 ml of TSC (1% SC, 0.05% CA) were added to this mixture. The solution was stirred vigorously for 15 minutes and then cooled to room temperature and centrifuged (20 minutess, 6,000 rpm) to remove excess TSC.

The pellet was re-dispersed in nanopure water. The GNPs concentration was measured using UV-Vis spectra (Figure S1).

Preparation of DNA/PEG functionalized gold nanoparticles

Gold nanoparticles were functionalized with thiolated DNA, DNA/PEG polymers. Prior to use, the SH-DNA was cleaved by the addition of CTEP and incubated at room temperature for 1 hour. The cleaved oligonucleotides were purified using a G-25 column. Freshly cleaved oligonucleotides were added to gold nanoparticles with different molar ratios (800:1, 400:1, 200:1 and 100:1). 0.01% sodium dodecyl sulfate (SDS) was added to 200:1 and 100:1 gold nanoparticle solutions. The oligonucleotide/gold nanoparticle solution was allowed to incubate at room temperature for 1 hour. The concentration of NaCl was increased to 50mM, using 2M NaCl, 0.01 M PBS, during a 12-hour period of time. Then, excess SH-PEG was added to the solution and it was incubated overnight at room temperature. To remove excess DNA and PEG, the gold nanoparticles were centrifuged and the supernatant was removed, leaving a pellet of gold nanoparticles at the bottom. The particles were then suspended in a PBS buffer containing 20 mM of NaCl. This washing process was repeated three times, and then the gold nanoparticles were dispersed in a PBS buffer and measured by UV-vis.

AFM characterization of DNA origami/GNP assemblies

5 ul of a sample solution were spotted onto freshly cleaved muscovite mica (Ted Pella inc) and absorbed for approximately 3 minutes. To remove buffer salts, doubly distilled H_2O (20-30ul) was placed on the mica, the drop was wicked off, and the sample was dried with compressed air. Atomic force imaging was done by utilizing Nanoscope III (Digital Instruments) tapping in air, with ultra-sharp 14 series (NSC 14) tips that had been purchased from MikroMasch (WWW. SPMTIPS.com).

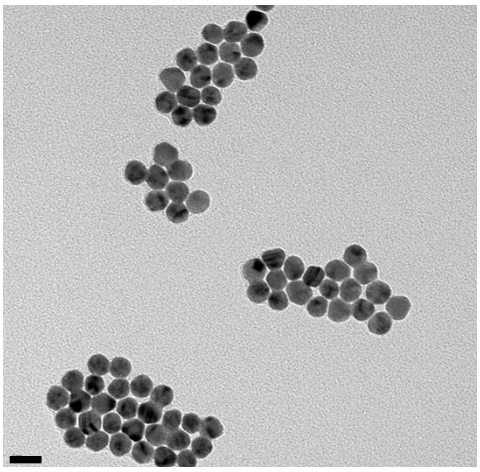


Figure S1. TEM image of synthesized 15 nm of gold nanoparticles (GNPs). Scale bar is 20nm.

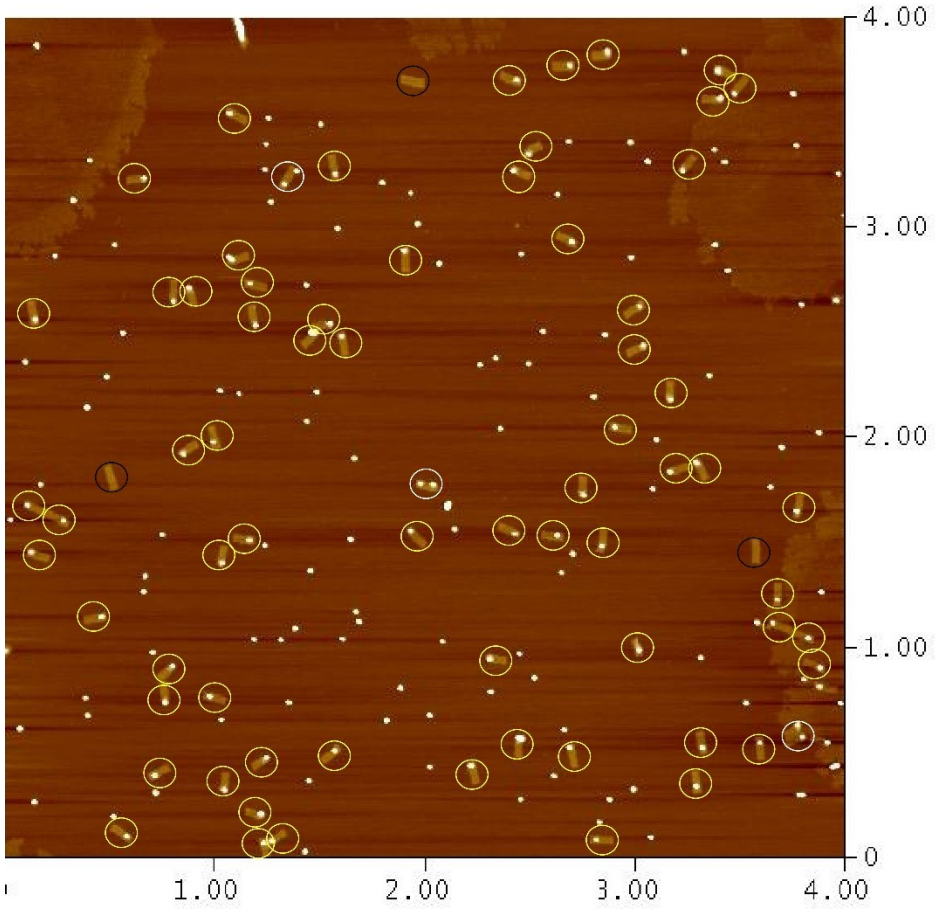
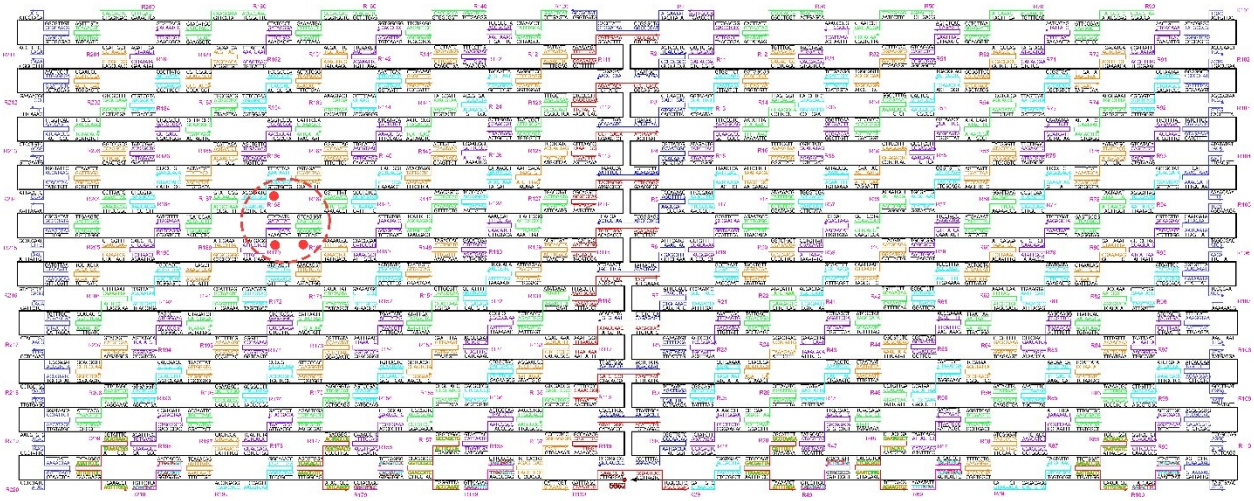


Figure S2. An example of an AFM image used to calculate the yield of GNP_{200p}/DNA origami assemblies. The yellow circles represent a DNA origami attached with a single GNP; the black circles represent the DNA origami without a GNP attachment; and the white circle represents the non-counted DNA origami. The final yield is the average yield of each image.

The equation used to calculate the hybridization yield of GNP/DNA origami assemblies was:

$$\%\ yield = \frac{number\ of\ DNA\ origami\ with\ single\ GNP\ attachment}{total\ number\ of\ DNA\ origami} x\ 100$$

The design and sequences of DNA origami



The design of DNA rectangular origami and the unmodified staple strands are same as reference S3. The modified sequences starting from 5' are listed as below:

D168-center:
AAAAAAAAAAAAAAAAAAAAAAAAAAGTTGCTTTTTTGATATATTATAGTCAGAAGC
TCGTTTAC
D169-center:
AAAAAAAAAAAAAAAAAAAAAAAAAAGTTGCTTACCCTGACAGAGGTCATTTTTGCG
GGTCAATA
D170-center:
AAAAAAAAAAAAAAAAAAAAAAAAAAGTTGCTTCAAAAACAAGCTATATTTTCATTT
ATTGCTCC

References:

1) P. W. K. Rothemund, Nature, 2009, 440, 297-302.

2) D. Ghosh, D. Sarkar, A. Girigoswami and N. Chattopadhyay, Journal of Nanoscience and Nanotechnology, 2010, 10, 1-6.

3) R. Wang, N. Colin, and S. Wind, Angew. Chem. Int. Ed, 2012, 51, 11325-11327