

Supporting Information

Water flattens graphene wrinkles: laser shock wrapping of graphene onto substrate-supported plasmonic nanoparticle arrays

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1. Experimental Section

1.1 Synthesis of gold nanospheres, nanorods and bipyramids

All solutions were prepared fresh for each synthesis using deionized (DI) water, except for the hydrogen tetrachloroaurate(III) (Sigma, No.520918), which was prepared as a 25 mM stock solution from a dry ampule and stored in the dark.

(a) *Gold nanospheres*: 1mL of 25mM HAuCl₄ was added to 90 mL of DI water at room temperature. After stirring for 1 min, 2.00 mL of 38.8 mM sodium citrate was added. One minute later, 1.00 mL of fresh 20mM NaBH₄ in 38.8 mM sodium citrate was added. The colloidal solution was stirred for an additional 5 min and stored in a dark bottle at 4 °C. This processes produces less than 3nm gold seed nanoparticles. For larger nanoparticle, 0.2 mL of 25mM HAuCl₄ was mixed with 15 mL DI water, then the solution was boiled. Subsequently, 0.07mL of 38.8 mM sodium citrate and the seed nanoparticle were added and stirred vigorously for 15 min. The solution was cooled down to room temperature and kept in at 4 °C. The gold nanosphere is 30±3 nm in diameter.

(b) *Gold nanorods*: For gold nanorods, an aliquot of the stock solution was diluted to 10 mM immediately before use. Gold seed particles were prepared by adding 250 μL of 10 mM hydrogen tetrachloroaurate(III) to 7.5 mL of 100 mM cetyltrimethylammonium bromide (CTAB) (Sigma, #H9151) in a plastic tube with brief, gentle mixing by inversion. Next, 600

μL of 10 mM sodium borohydride (Acros, #18930) was prepared from DI water chilled to 2–8 °C in a refrigerator and added to the seed solution immediately after preparation, followed by mixing by inversion for 1–2 min. The pale brown seed solution was stable and usable for several hours. For scale-up of the nanorods, the procedure in the step of growth solution was slightly modified and prepared by adding the following reagents to a plastic tube in the following order and then gently mixing each by inversion: 500 mL of 100 mM CTAB, 20 mL of 10 mM hydrogen tetrachloroaurate(III), and 3 mL of 10 mM silver nitrate (Acros, #19768). Next, 3.3 mL of 100 mM ascorbic acid (Fisher, #A61) was added and mixed by inversion, which changed the solution from brownish-yellow to colorless. To initiate nanorod growth, 6 mL of seed solution was added to the growth solution, mixed gently by inversion, and left still for three hours. During this time, the color changed gradually to dark purple, with most of the color change occurring in the first hour. Gold nanorod has an average length of 40 ± 2.5 nm and an average width of 12 ± 1 nm.

(c) Gold bipyramids: Sodium citrate-stabilized gold seed particles were prepared for the synthesis of gold bipyramids. Typically, a 20 mL solution of 0.125 mM hydrogen tetrachloroaurate(III) and 0.25 mM sodium citrate (Fisher, No. S279) were prepared and mixed briefly. Next, 0.3 mL of fresh and ice-cold aqueous 10 mM NaBH_4 (Acros, No. 18930) solution prepared at room temperature was added, followed by mixing for 2 min. The resulting gold seed solution was kept at room temperature for at least 2 h for complete reaction. Then, the dark pink seed solution was stable and usable for gold bipyramid growth. Next, 0.5 mL of 10 mM hydrogen tetrachloroaurate(III) and 10 mL of 100 mM cetyltrimethylammonium bromide (CTAB) (Sigma, No. H9151) were mixed with 0.1 mL of 10 mM silver nitrate (Acros, No. 19768) for the preparation of the growth solution. Then, 0.2 mL of 1.0 M hydrochloric acid (Hampton Research, No. HR2-581) and 0.08 mL of 100 mM L-ascorbic acid (Fisher, No. A61) were added to the solution in order. Finally, the seed solution was added to the growth solution. The volume of seed solution was varied between

15 and 50 μL to synthesize different sizes of gold bipyramids. These solutions were kept at 28 $^{\circ}\text{C}$ for several hours. During this time, the color changed gradually from almost clear to dark pink, with most of the color change occurring in the first hour. Gold bipyramids yield an average length 117 ± 3 nm and an average width of 48 ± 2 nm.

1.2 Gold Nanoparticles PEGylation

1 mL of gold nanospheres was centrifuged at 8000 rpm for 20 min and the solution was decanted and the pellet on the bottom of the tube was redispersed in 1 mL of DI water. Next, 0.015 mL of 1 mM thiol terminated methoxypoly(ethylene glycol) (mPEG-SH, 5000 MW, RAPP Polymere) was added to the solution, then it was left for 2 hours. Subsequently, the centrifuge/decant cycles were carried out at least one more time and the nanospheres were resuspended in 1 mL of DI water. In case of gold nanorods and bipyramids, 1 mL of the gold nanoparticles solution with 0.1 mL of 2 mM potassium carbonate was centrifuged at 7000 rpm for 30 min to pellet the nanoparticles. The suspended solution was decanted, and the pellet was resuspended in 1 mL of DI water with 0.01 mL of 1 mM mPEG-SH. This solution was shaken briefly by a vortex mixer. Then, the solution was left overnight to displace the CTAB. Thereafter, the solution was centrifuged under the same condition again. The nanorods were then taken through at least one more centrifuge/decant cycles, resuspending each time in deionized water, to further reduce the CTAB concentration.

1.3 Gold Nanoparticles Substrate Fabrication

Glass microscopic slides (75 mm \times 25 mm) were cleaned in piranha solution (3:1 H_2SO_4 /30% H_2O_2), thoroughly rinsed with deionized water, and dried. They were then immersed in an ethanolic solution of 10% aminopropyltriethoxysilane (APTES) (Sigma, #440140) overnight, rinsed with water, and dried. The APTES coated slides were then immersed in a PEGylated nanoparticles solution for 24~36 hours. Once rinsed and dried, a uniform layer of gold

nanorods remained on the surface with an absorbance of approximately 0.1 at the LSPR peak wavelength. To remove the mPEG-SH and other contaminants, the substrates were processed in an oxygen plasma cleaner at low power for 2 min in 100 mT oxygen (Branson Plasma Asher) and cleaned by fuzzing nitrogen gas.

2. Supporting Figures

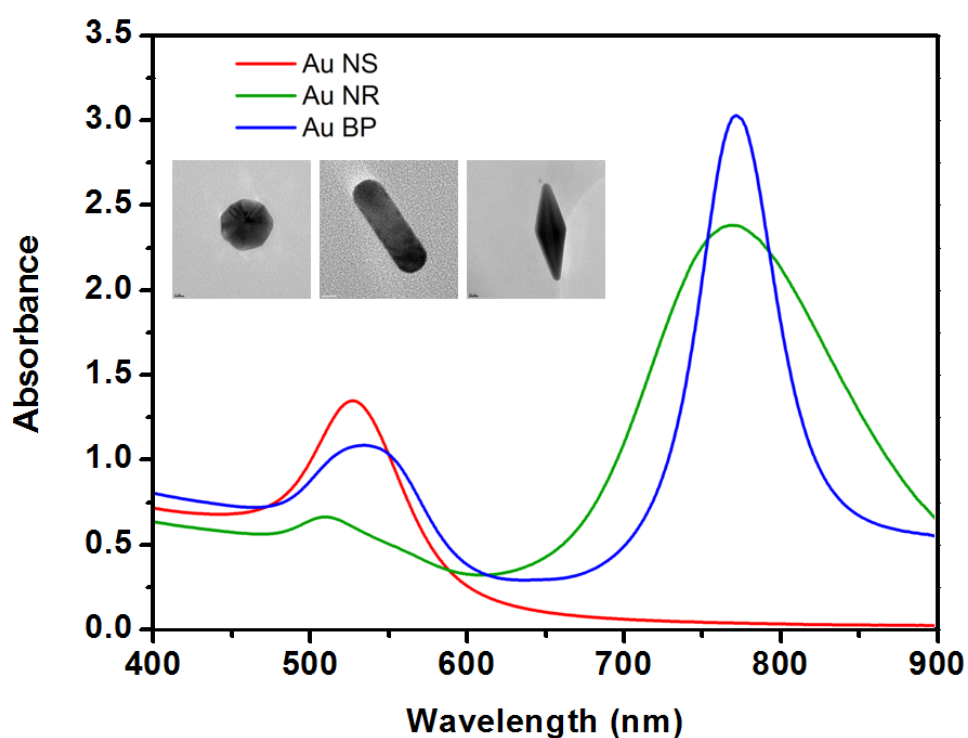


Figure S1. Absorption spectra of Au NS, Au NR and Au BP.

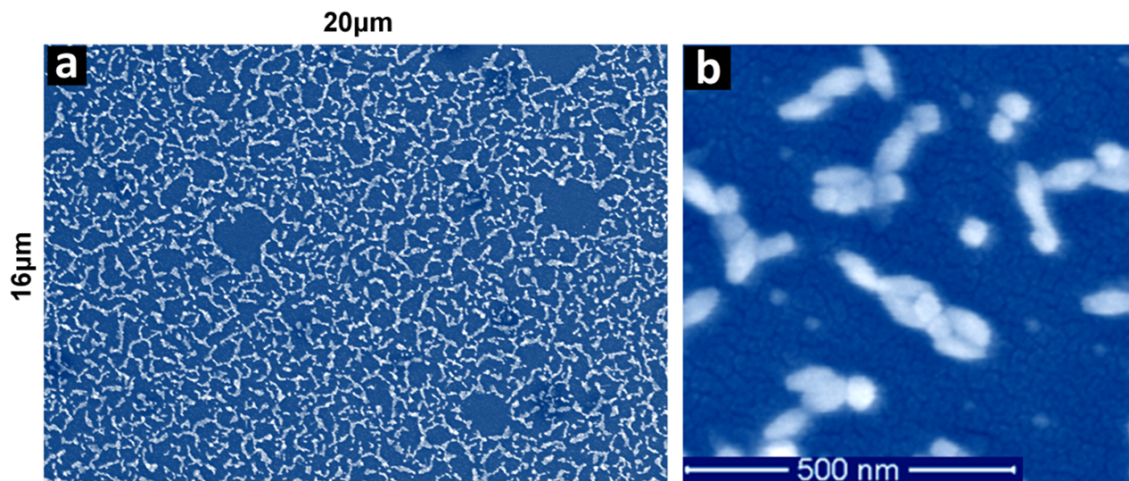


Figure S2. FESEM image of Au BPs on glass substrate (a) large area image and (b) high resolution image.

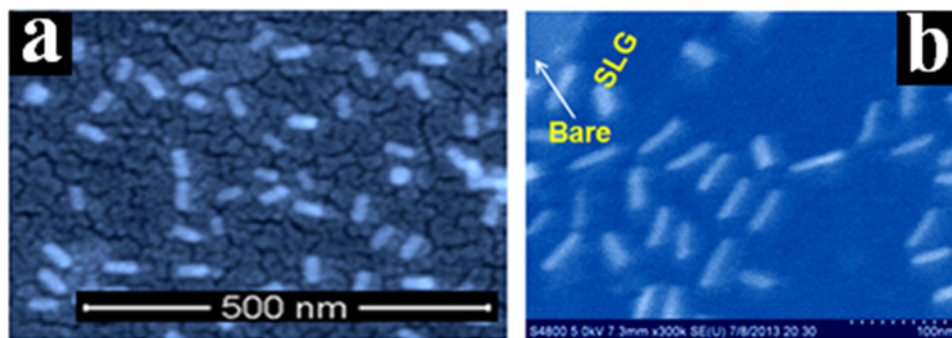


Figure S3. FESEM image of (a) Au NR on glass substrate, (b) single layer graphene on Au NRs.

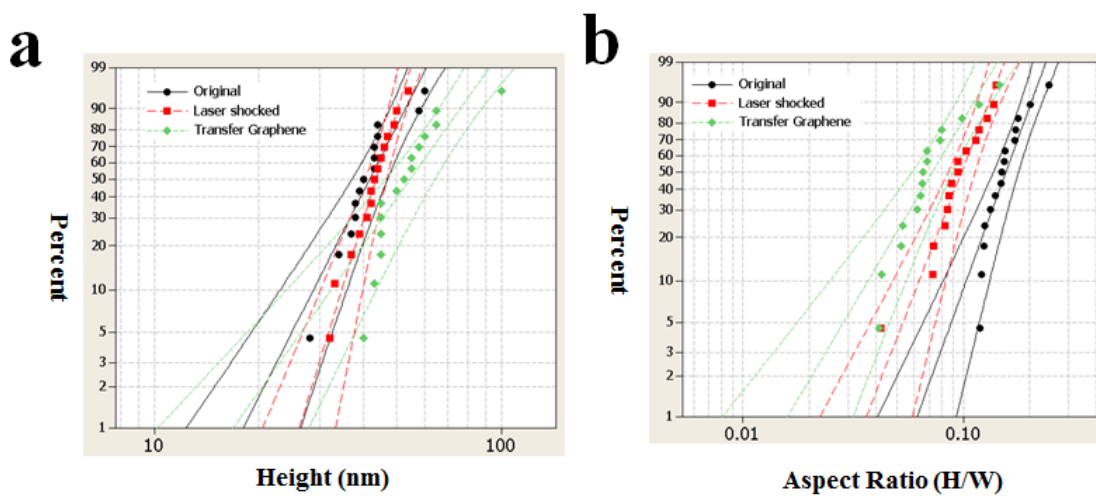


Figure S4. Probability plot of height (a) and aspect ratio (b) of Au nanoparticles on the original sample with wet-transferred graphene and after LSW.

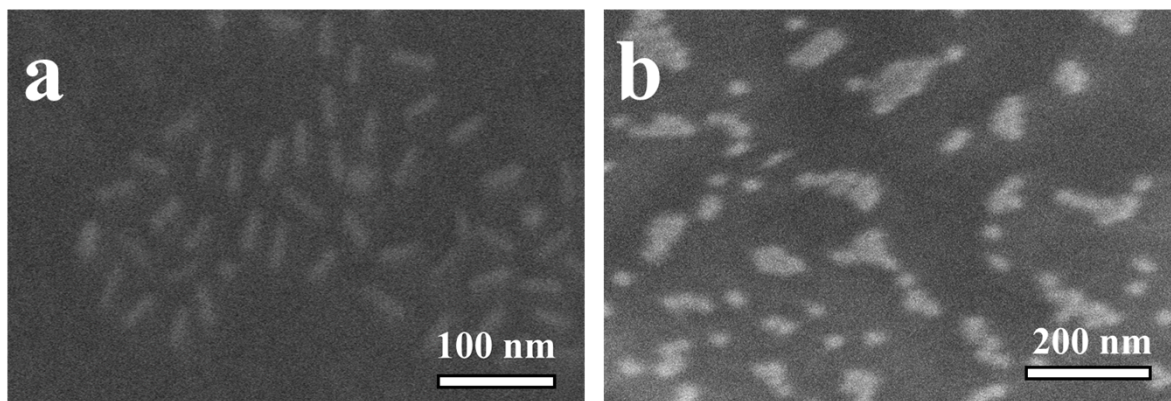


Figure S5. FESEM images of LSW of single layer graphene onto glass substrate supported Au NRs (a) and Au BPs (b).