Highly Conductive Ribbons Prepared by Stick-Slip Assembly of Organosoluble Gold Nanoparticles

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Synthesis of dodecanethiol stabilized gold nanoparticles by the one phase method (Au NP-1).
Dodecanethiol stabilized gold nanoparticles (Au NP-1) with an average size of 5.3 nm were prepared according to the method reported by Zheng et al.[17] Au(PPh$_3$)Cl was prepared by dropwise addition of triphenylphosphine (3.6 mmol) to HAuCl$_4$.3H$_2$O (1.8 mmol) in ethanol (5 mL). The product was filtered, washed with ethanol, precipitated from acetone/THF (1:1), filtered and dried to obtain a white powder (yield: 70%). Recrystallization from dichloromethane-pentane mixtures was followed by washings to give the pure compound as white, transparent needles (yield: 58%). Au NPs were prepared by dissolving Au(PPh$_3$)Cl (0.25 mmol) and 125 μL of dodecanethiol in dry toluene (20 mL) in a round-bottom flask. *Tert*-butyl amine borane complex (2.5 mmol) was added swiftly with vigorous stirring. The mixture slowly changed colors from light yellow to deep red, purple in 2 minutes. The mixture was heated in an

oil bath preheated at 50°C for 5 minutes under slow stirring. The Au NP solutions was concentrated under a stream of $N_{2(g)}$, then precipitated in cold ethanol and collected by centrifugation. The NPs were purified twice by washings with chloroform:acetone (1:90 v/v) followed by centrifugation at 5 krpm for 15 min. The precipitate was collected and redissolved in toluene.

Synthesis of dodecanethiol stabilized Au NPs by the two-phase method (Au NP-2). Dodecanethiol stabilized Au NPs (Au NP-2) with an average size of 4 nm were prepared with minor modifications of the Brust two-phase method.[12] Hydrogen tetrachloroaurate (III) trihydrate (HAuCl$_4$.3H$_2$O, 33 mg) solution in water (3 mL) was added to a solution of tetraoctylammonium bromide (TOAB, 0.21 g) in toluene (8 mL). The mixture was stirred vigorously until the aqueous solution became colorless; then the Au complex was transferred to the organic phase. The organic solution was separated and stirred with dodecanethiol (5 μL). A cold (0 °C) aqueous solution of sodium borohydride (36 mg in 2 mL) was injected swiftly to the vigorously stirred solution. The solution immediately turned dark purple, and was stirred for 2 h at room temperature. Toluene was evaporated to ~3 mL by applying a gentle stream of $N_{2(g)}$, and the Au NPs were precipitated in cold ethanol and collected by centrifugation. The NPs obtained were purified further by washings with CHCl$_3$:acetone (1:90 v/v), followed by centrifugation at 5 krpm for 15 min. After the second centrifugation cycle (10 min, 5 krpm), trace Au NP remained in the supernatant. The precipitants were collected (yield: 50%) and redissolved in toluene.

Synthesis of dodecylamine stabilized Au NPs by the one-phase method (Au NP-4). Dodecylamine-stabilized Au NPs (Au NP-4) with an average diameter of 3.3 nm were prepared by modification of the method reported by Polavarapu.[22] Hydrogen tetrachloroaurate (III) trihydrate (HAuCl$_4$.3H$_2$O, 25 mg) was dissolved in toluene (10 mL). Dodecylamine (DDA, 0.5

mL) was added, the solution was stirred vigorously, and combined with a cold (0 °C) aqueous solution of sodium borohydride (2.5 mL, 10 mg/mL). The solution was stirred for 5 min, washed with water, and the organic solution was separated. Toluene was evaporated to ~1 mL by applying a gentle stream of $N_{2(g)}$ and the Au NPs were precipitated in cold ethanol and collected by centrifugation. The NPs obtained were purified by this washing procedure twice, and the precipitate was collected and redissolved in toluene.

Flow coating of Au NPs. The flow coating instrument consists of an 80 μm thick PET film blade attached to a vertical translation stage with rotational alignment arms. Bending ribbon parallel to the substrate was made by scoring at a distance of 1 mm from the edge of coating blade to stabilize film bending. The glass substrate was fixed to a linear translation stage controlled by a servo motor (Parker Daedal, Cleveland, OH). The blade was positioned at an angle of 40° from horizontal surface along the translation axis, and brought into slight contact with the substrate. The Au NP solution in toluene (1.0 mg/mL, 5 μL) was injected slowly to fill the capillary opening between the blade and substrate surface. Once the solution was held by capillary forces under the blade, the stage was translated with a velocity of 1.5 mm/s, 100 ms – 1 s stopping time and ribbon spacing of 30 μm. The stage translation was controlled by a computer interface (LabView, National Instruments, Austin, TX).

Characterization. UV-Vis spectra of the NP solution were recorded on a Perkin Elmer Lambda 25 spectrophotometer. Infrared (IR) spectra were obtained on a Perkin-Elmer Spectrum One FTIR spectrometer equipped with an ATR accessory. ^{1}H and ^{31}P NMR spectra were recorded using Bruker Spectrospin 300 spectrometer operating at the appropriate frequencies using solvent residual peak as internal reference. X-ray Photoelectron Spectroscopy (XPS) spectra were recorded on a Physical Electronics Quantum 2000 spectrometer with Al KR excitation at a

spot size of 100 μm at 25 W. XPS samples were prepared by drying a drop of concentrated gold nanoparticle solution on clean Si wafer. XPS spectra were obtained at 75° takeoff angles with respect to the plane of the sample surface. Transmission electron microscopy (TEM) was performed on a JEOL 200CX microscope. TEM grids (3-4 nm amorphous carbon film supported on 400-mesh copper grid) were purchased from Ted Pella, Inc. TEM samples were prepared by drop casting Au NP solution onto carbon coated grid and drying the grid at ambient atmosphere. The organic content (weight percent organic) of the Au NPs was determined by thermogravimetric analysis (TA Instruments, dynamic scans under N_2, heating rate of 10 °C/min from 50 to 650 °C). The dimensions of the Au NP ribbons were characterized by atomic force microscopy (Nanoscope III, Digital Instrument Co., Santa Barbara, CA) in tapping mode. AFM images were processed with software for 1st and 2nd order flattening and further analysis. Scanning electron microscopy of flow-coated ribbons was performed on a Magellan FX II microscope.

Sintering Au NP ribbons. Thermal sintering of Au NP ribbons was carried out by placing the samples on pre-heated hotplate (240 °C) for 5 min.

Conductivity measurement. Conductivity measurement was carried out using a Keithley 4200-SCS using two point- and four point-probes. Dual sweep was performed from −1 V to 1 V and repeated at least three times using different sweep rates (10 to 30 mV/s) to confirm signal hysteresis. Conductivity values of the Au NP ribbons were calculated from the resistance of parallel Au NP ribbons between Au IDE fingers using the general resistivity formula and the dimensions of the ribbons. AFM conductivity measurements were obtained with an Asylum Research MFP-3D atomic force microscope. The AFM is equipped with an ORCA module consisting of a conducting cantilever holder and sample mount. Silicon AFM tips with a 25 nm

platinum coating, purchased from AppNano (model ANSCM-PT, nominal radius 30 nm; spring constant 3 N/m; resonance frequency 62 kHz), were used. Images were recorded at room temperature in AC tapping mode and used as a map. The tip was then placed at a desired location and put into contact mode at a set point voltage of 0.2 V. Current-voltage plots were acquired with a voltage bias range of -1 V to 1 V or -3 V to 3 V.
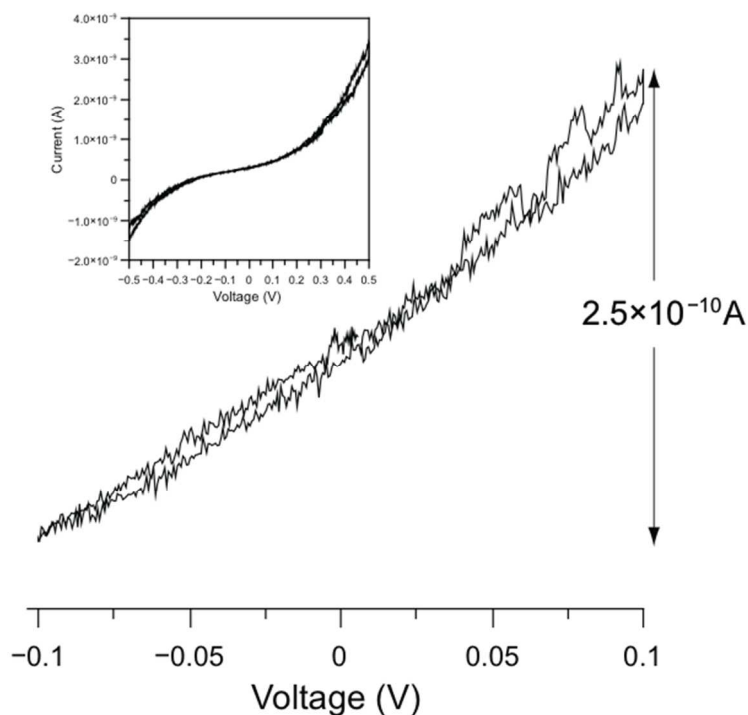

Figure SI-1. Current-voltage plot of single Au NP-1 ribbon measured across 0.2 V potential window using conductive AFM. Inset shows nonlinear current response across 1 V potential window.

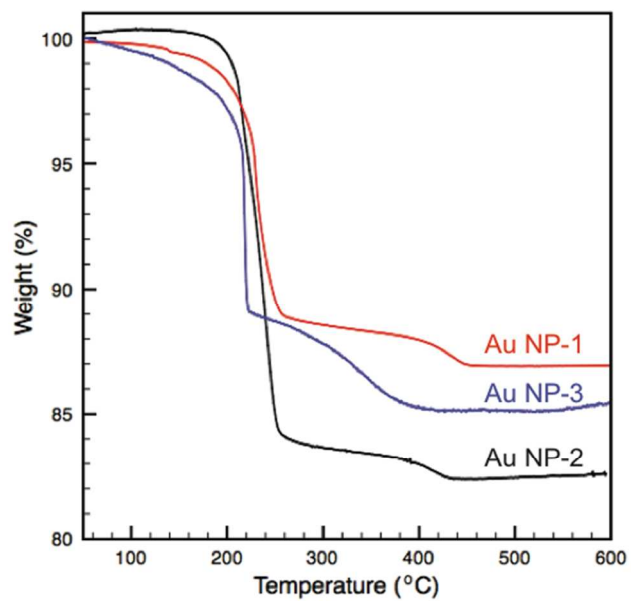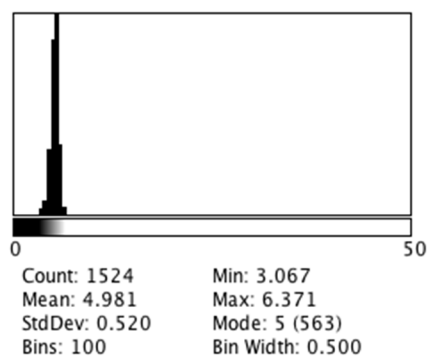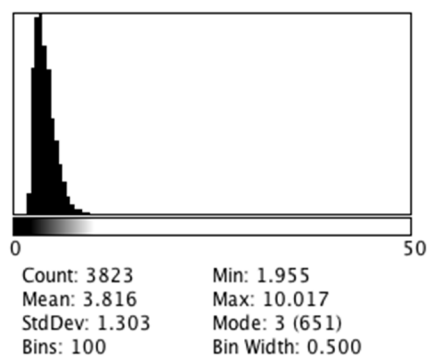**TGA analysis of dodecanethiol covered Au NP samples**

Figure SI-2. TGA profile of Au NP-1, Au NP-2 and Au NP-3
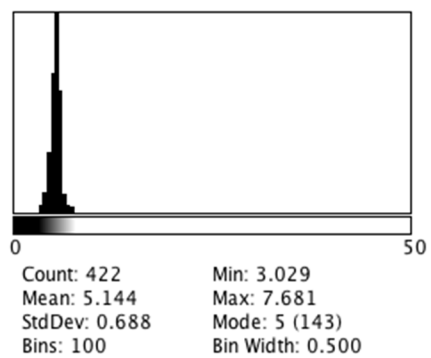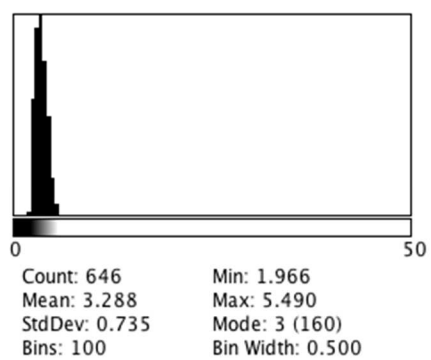
Size distribution of Au NP samples

Au NP-1

Count: 1524   Min: 3.067
Mean: 4.981   Max: 6.371
StdDev: 0.520   Mode: 5 (563)
Bins: 100   Bin Width: 0.500

Au NP-2

Count: 3823   Min: 1.955
Mean: 3.816   Max: 10.017
StdDev: 1.303   Mode: 3 (651)
Bins: 100   Bin Width: 0.500

Au NP-3

Count: 422	Min: 3.029
Mean: 5.144	Max: 7.681
StdDev: 0.688	Mode: 5 (143)
Bins: 100	Bin Width: 0.500

Au NP-4

Count: 646	Min: 1.966
Mean: 3.288	Max: 5.490
StdDev: 0.735	Mode: 3 (160)
Bins: 100	Bin Width: 0.500

XPS analysis of Au NP samples

Table SI-1. XPS analysis of dodecanethiol covered Au NPs. Phosphor and bromine in the reaction byproducts or excess ligands were not detected (below detection limit).

[mol%]	Au	C	S	**C/S**
Au NP-1	17.2	79.1	3.5	**22.6**
Au NP-2	17.3	79.7	2.8	**28.5**
Au NP-3	22.9	74.6	2.3	**32.4**

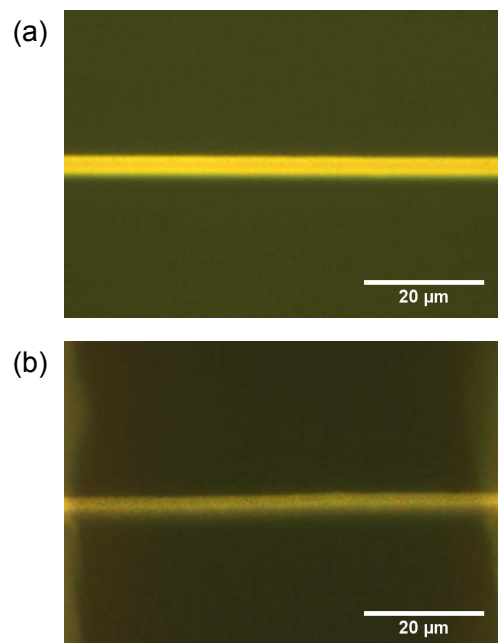**Optical microscopy images of Au NP + PS (Au NP-5) ribbons**

Figure SI-3. Optical microscopy images of Au NP-5: (a) before thermal annealing, (b) after thermal annealing (240 °C, 5 min).

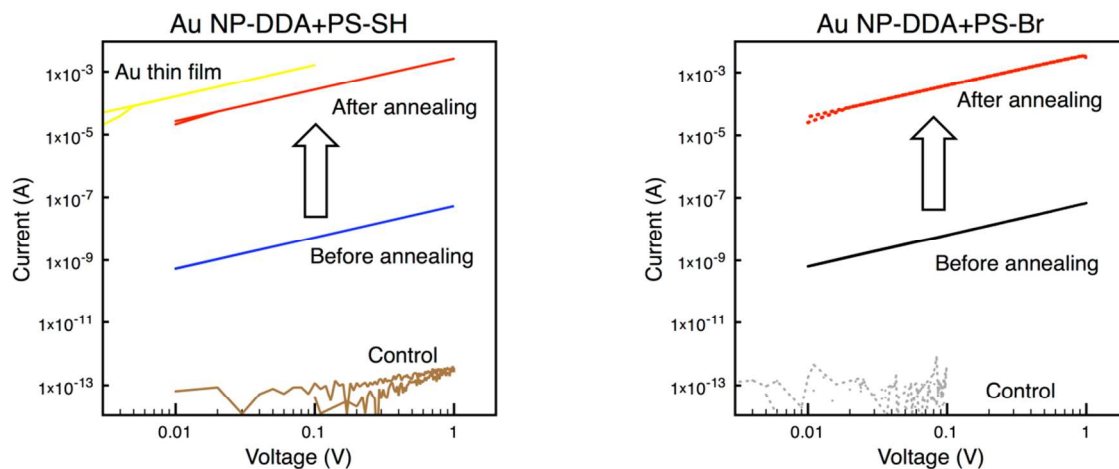**Comparison of thermally annealed Au NP ribbons added with functional and non-functional polymers**
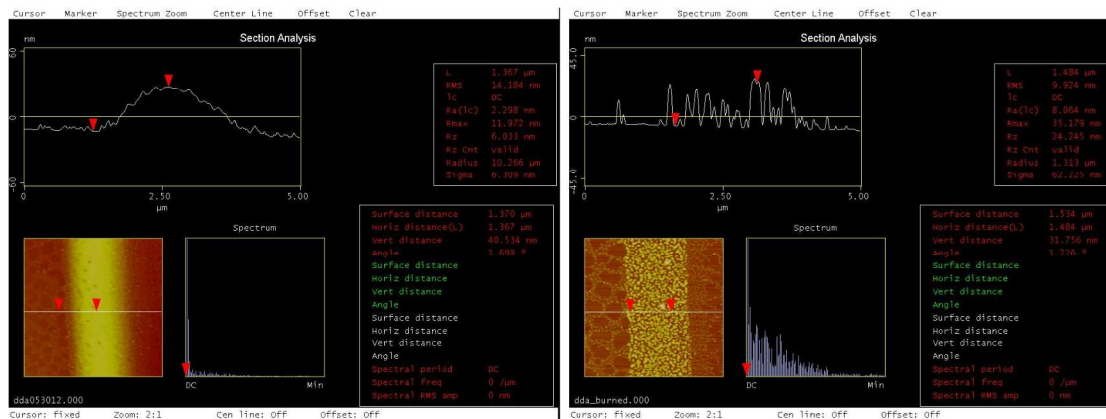

Figure SI-4. Comparison of I-V response between thermally annealed Au NP ribbons that were prepared from Au NP solutions added with thiol terminated polystyrene (left) and non-functional polystyrene (right)

Comparison of Au NP-4 ribbons and Au NP-5 ribbons, before and after thermal annealing

Au NP-4 (Au NP-DDA)
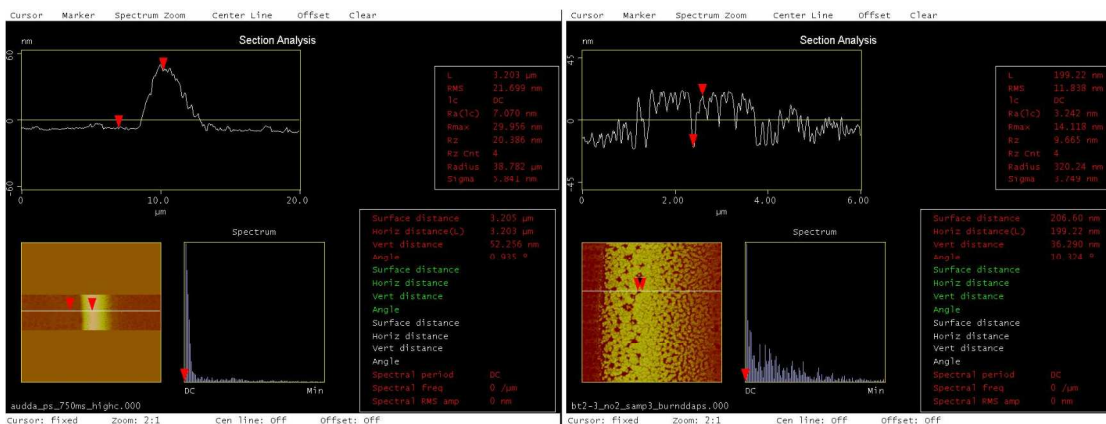

Au NP-5 (Au NP-DDA+PS-SH)

Figure SI-5. AFM cross section images of Au NP ribbons before (left) and after (right) thermal annealing: (top) Au NP-4, (bottom) Au NP-5