Supporting Information

Optimally Functionalized Adhesion for Contact Transfer Printing of Plasmonic Nanostructures on Flexible Substrate

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Keywords

Self-Assembled Monolayer, Contact Transfer Printing, Adhesion Energy, Nanoplasmonic Structure, Polar Surface Energy, Dispersive Surface Energy

Experimental Methods

Materials: 3-Mercaptopropionic acid (3-MPA, 99%), 11-Mercaptodecanoic acid (11-MUA, 98%), 16-Mercaptohexadecanoic acid (16-MHA, 90%), 1,2-Ethanedithiol (1,2-EDT, 98%), 3,6-dioxa-1,8-octanedithiol (3,6-DODT, 95%) and 1,8-Octanedithiol (1,8-ODT, 97%) were used as different types of adhesion layers and purchased from Sigma-Aldrich. The 1,10-Decanedithiol (1,10-DDT, 95%) was purchased from Alfa Aesar and also used as an adhesion layer. The ethanol was used as a solvent and purchased from J. T. Baker solutions. The tricholoro(1H, 1H, 2H, 2H-perfluorooctyl)silane (FOTS) was purchased from Sigma-Aldrich and its role was an anti-adhesion layer for releasing a metal from a silicon mold. The high quality flexible substrate of PET was purchased from Graphene platform (188 μm thickness, 92% light transmission with 0.9% haze, coefficient of thermal expansion in the longitudinal direction (MD) 0.9% and transverse direction (TD) 0.7%). The 150 nm nanoparticles are purchased from BBI international. The copper (II) sulfate solution of 0.1 M (Sigma-Aldrich) was used for linking the 150 nm nanoparticles with printed nanostructure to investigate the plasmon coupling effect.

Fabrication of nanoscale silicon mold: The silicon mold was made by the maskless photolithography with I-line (365 nm wavelength) (NanoSystem Solutions, Inc. D-LIGHT DL-1000). By using a maskless lithography, we fabricated a 1 μm sized micro pattern with AZ5214 photoresist on the silicon. The 100 nm thick gold film was deposited on the micro pattern by thermal evaporation. After that, the photoresist was removed by Acetone. A nanoscale silicon mold was further fabricated from the micro-scaled gold pattern by using a non-Bosch etching process. The non-Bosch etching process is etching of the silicon without the formation of passivation layer so the etched shape is not anisotropic. By using this condition, we have achieved the nanoscale silicon mold by over etching the side wall of the silicon. The optimal gold mask layer was 100 nm with 3 μm pitch. The etching gas and their flow rates were O_2 (10 sccm), SF_6 (40 sccm), N_2 (20 sccm), and He (1000 sccm), respectively. The pressure of the chamber was 10 mTorr. The scale of the nanostructures used in this experiment ranged from 500 nm to 550 nm.

Condition of the FOTS coating on silicon mold: The FOTS layer plays a role of anti-adhesion layer for releasing and transferring the metal to the flexible substrate. To make a FOTS layer, the 30 μl FOTS was prepared in the desiccator. When the desiccator chamber was changed to the vacuum state, the FOTS was vaporized and deposited on the silicon mold for 2 hours. This layer was prepared with a self-assembled monolayer with 2-3 nm thickness as shown in Transmission electron microscopy (TEM) image in reference [1].

Deposition of gold on the silicon mold-FOTS layer: The thermally evaporated gold was deposited on the silicon mold-FOTS layer with 100 nm thickness. The gold was deposited for 500 s with the deposition rate of 2.0 Å/s.

Preparation of the solutions for making a functionalized gold nanostructure: To make a functionalized nanostructure, we have prepared the chemical solution for functionalization on the gold nanostructure. The 3-MPA, 11-MUA, 16-MHA were used for functionalization of the mercapto alkyl carboxylic acid on the gold. The 1,2-EDT, 3,6-DODT, 1,8-ODT and 1, 10-DDT were used for functionalization of the alkyl dithiol. All chemical reagent were prepared in

ethanol solution with 1 mM. The 3-MPA, 1,2-EDT, 3,6-DODT, 1,8-ODT and 1, 10-DDT are liquid type chemical reagents. So these chemical reagents were directly added to the 50 ml ethanol. The 11-MUA and 16-MHA are powders so the additional stirring in 200 rpm was conducted for 30 min in 50 ml ethanol solution. The prepared gold nanostructure on the silicon mold was immersed in the solution for 12 hours at room temperature. After 12 hours, the cleaning step was followed with pure ethanol and deionized water and then drying step was gently applied with purge nitrogen gas.

Transfer printing of functionalized gold nanostructure: For making a nanostructure on flexible substrate, we have used the contact transfer printing method. First, we have prepared a hot plate. On the hot plate, we have placed the silicon mold prepared with FOTS layer and functionalized nanostructure and then placed the flexible substrate, PET, on the silicon mold. The temperature of the hot plate was set to 80℃ for 30 min and then 100℃ for 2 hours. The pressure was applied on the flexible substrate with 0.56 psi. As the purpose of the pressure was to keep the flexible substrate on the silicon mold, the pressure level in our experiment was much smaller compared to other transfer printing methods using 194 kPa or 500 psi [2, 3]. So the transfer printing of functionalized nanostructure does not rely critically on the pressure control. After 2 hours and 30 min, we have detached the flexible substrate from the silicon mold. In this process, the FOTS layer plays a role of releasing the nanostructure to the flexible substrate. Functionalization on the nanostructure serves as an adhesion layer for the nanostructure to attach on the flexible substrate. Also, this layer functionalized on the top as well as side edge of the gold nanostructure works as a functionalized terminal for interacting with bio or chemical molecules.

Characterization: The surface morphologies of the transfer printed nanostructure on the flexible substrate were observed by using the field emission electron microscopy (FE-SEM) (JEOL, JSM-7100F). To investigate the light scattering from the transfer printed nanostructure on the flexible substrate, we have used the Inverted optical microscope (Nikon, Ti-U) with a dark-field condenser (NA = 0.80–0.95, Dry type) and digital camera (Nikon, DS-Ril). From this system, we can identify the scattering of nanostructure on PET substrate. The halogen lamp with a neutral color balance filter is used as a light source in the optical measurement.

To measure the spectra from the nanostructure, we have used the spectrophotometer (Dong Woo Optron Co., Ltd, Monora 320i) with a charge-coupled device (CCD) (Andor Technology, DV420A-BV) which was connected to the inverted optical microscope. Using the dark-field images, we have calculated the yield of transfer printing by counting the number of nanostructures scattering light among the array of 20×20 nanostructures.

To characterize the surface tension and adhesion energy, we have used a contact angle (CA) measurement system (Dataphysics, OCS15EC) with ultrapure DI water (72.2 mN/m), and ethylene glycol (47.3 mN/m) at room temperature by the sessile drop method. The microsyringe (Hamilton) with a microneedle (inner diameter of <0.1 mm) is used for dropping the 5 μl liquid to the target surfaces. By using software in the measurement system, we can calculate the dispersive and polar surface energies based on the measured contact angles.

To analyze the chemical composition on the functionalized gold nanostructure, we have used the X-ray photoelectron spectroscopy (XPS) from Thermo Fisher Scientific (K-ALPHA ESCA

SYSTEM) with monochromatic Al K_α X-ray source. The thicknesses of the 1,2-EDT, 3-MPA, 3,6-DODT, 1,8-ODT, 1,10-DDT, 11-MUA, and16-MHA have been measured by atomic force microscopy (AFM) (Park Systems, XE-100).

All the simulations were performed using the commercial software from Lumerical. In the simulation, a rectangular nanostructure (500 x 500 x 100 nm) is enclosed by perfectly matched layer (PML). The incident light is a plane wave and the angle of the plane wave is tuned from 0° to 60° for angled light. The Gaussian source along the z-direction is additionally specified. The monitoring line is set along the normal direction for measuring the cross-sectional field distribution. The dielectric function of gold is Au (Gold)-CRC from material library in the software.

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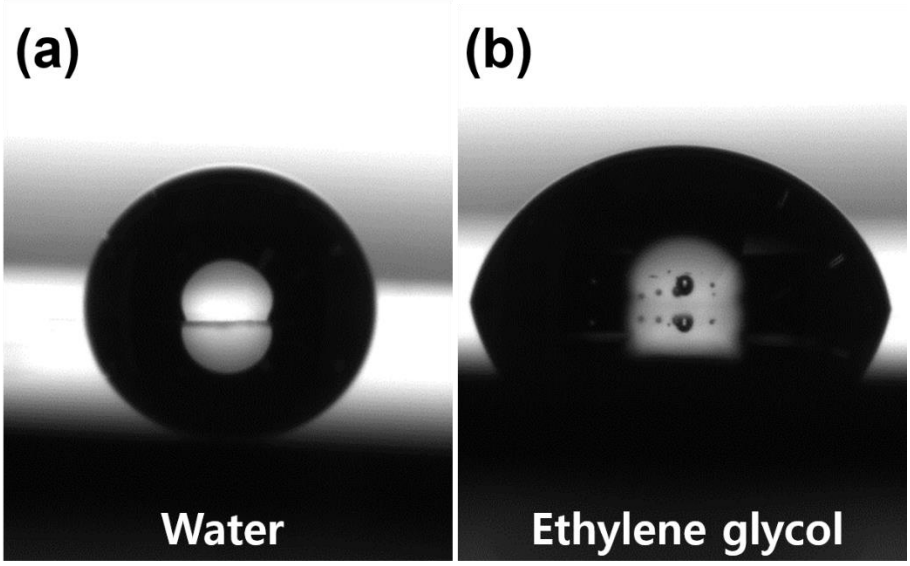

Figure S1. Contact angle of (a) water, and (b) ethylene glycol on FOTS surface.

The contact angle on the Trichloro(1H,1H,2H,2H-perfluorooctyl)silane (FOTS) is 101° (water) and 79° (ethylene glycol). From the measurements of contact angle, the dispersive and polar part of surface energy are calculated. The dispersive surface energy (γ^d) is 12.07 mJ/m^2 while the polar surface energy (γ^p) is 7.90 mJ/m^2. The dispersive and polar surface energy of gold surface are defined in Table S1. Based on the harmonic mean equation, the adhesion energy between the FOTS and gold surface is 49.2 mJ/m^2 which is the lowest value compared to the other adhesion. So it can be used as an anti-adhesion layer for transferring the gold nanostructure on the target substrate.

Table S1 Static contact angle measurement: Flat and nanostructured gold surface, flexible polymer substrates (PET, Kapton, and PS) and gold nanostructure array with functionalizations (3-MPA, 11-MUA, 16-MHA, 1,2-EDT, 3,6-DODT, 1,8-ODT, and 1,10-DDT). Wetting properties were investigated by contact angle, dispersion and polar component of surface energy, and total surface energy depending on the probing liquids (water and ethylene glycol). All averages and errors were calculated from five measurements (There are left and right sides of the contact angles on the solid surface so that the number of total angle data is 10.)

	Value		Flat gold	Rough gold	Kapton	PET	PS		
Flat Surface	Contact Angle (deg)	Water	85.6±5.6	76.0±0.5	66.0±0.5	62.4±0.4	75.0±0.7		
		Ethylene Glycol	58.1±1.2	51.0±0.5	44.0±0.5	63.4±0.2	60.0±0		
	Surface Energy	γ^d	17.5	16.2	14.9	5.3	10.2		
		γ^p	12.2	17.9	24.7	40.3	23.2		
		γ^{total}	29.7	33.9	39.7	45.6	33.4		
	Value		3-MPA	11-MUA	16-MHA	1,2-EDT	3,6-DODT	1,8-ODT	1,10-DDT
Flat Surface	Contact Angle (deg)	Water	49.6±2.2	67.6±2.5	68.3±4.0	78±2.5	56.0±7.4	82±3.2	85±2.0
		Ethylene Glycol	34.5±3.0	42.5±2.6	47.8±5.6	51±4.2	36.0±1.7	53±5.0	54±1.3
	Surface Energy	γ^d	13.6	16.5	16.9	17.32	15.06	18.88	20.88
		γ^p	37.6	22.6	20.3	16.08	31.11	13.19	10.87
		γ^{total}	51.2	39.1	37.2	33.40	46.17	32.07	31.75
Nanostructured Surface	Contact Angle (deg)	Water	13.8±0	18.3±0.6	23.5±0	68.0±0	54.0±0	70±1.5	71±1.6
		Ethylene Glycol	17.1±0	17.2±0.2	17.5±0	45.0±0	38.0±0	46±1.3	46.7±0.2
	Surface Energy	γ^d	13.0	13.2	13.7	15.3	13.5	15.76	15.87
		γ^p	61.5	59.1	55.6	23.2	34.5	21.68	20.99
		γ^{total}	74.5	72.3	69.2	38.6	48.0	37.44	36.86

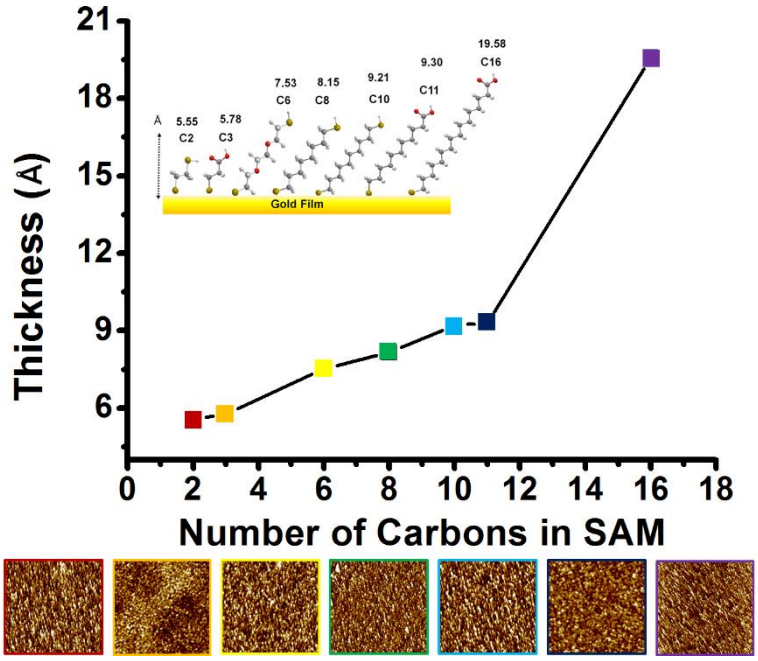

Figure S2. Thickness of self-assembled monolayer (SAM) measured by AFM. The functionalizations on gold surface are 1,2-EDT (C2), 3-MPA (C3), 3,6-DODT (C6), 1,8-ODT (C8), 1,10-DDT (C10), 11-MUA (C11), and 16-MHA (C16). (1×1 μm^2 size).

AFM data shows the SAM thicknesses of 1,2-EDT (C2), 3-MPA (C3), 3,6-DODT (C6), 1,8-ODT (C8), 1,10-DDT (C10), 11-MUA (C11), and 16-MHA (C16). The thickness of the SAM is increased as the length and the number of carbon atoms in alkyl chain are increased. This data is similar to the data in references measured by ellipsometry and AFM method [1-3].

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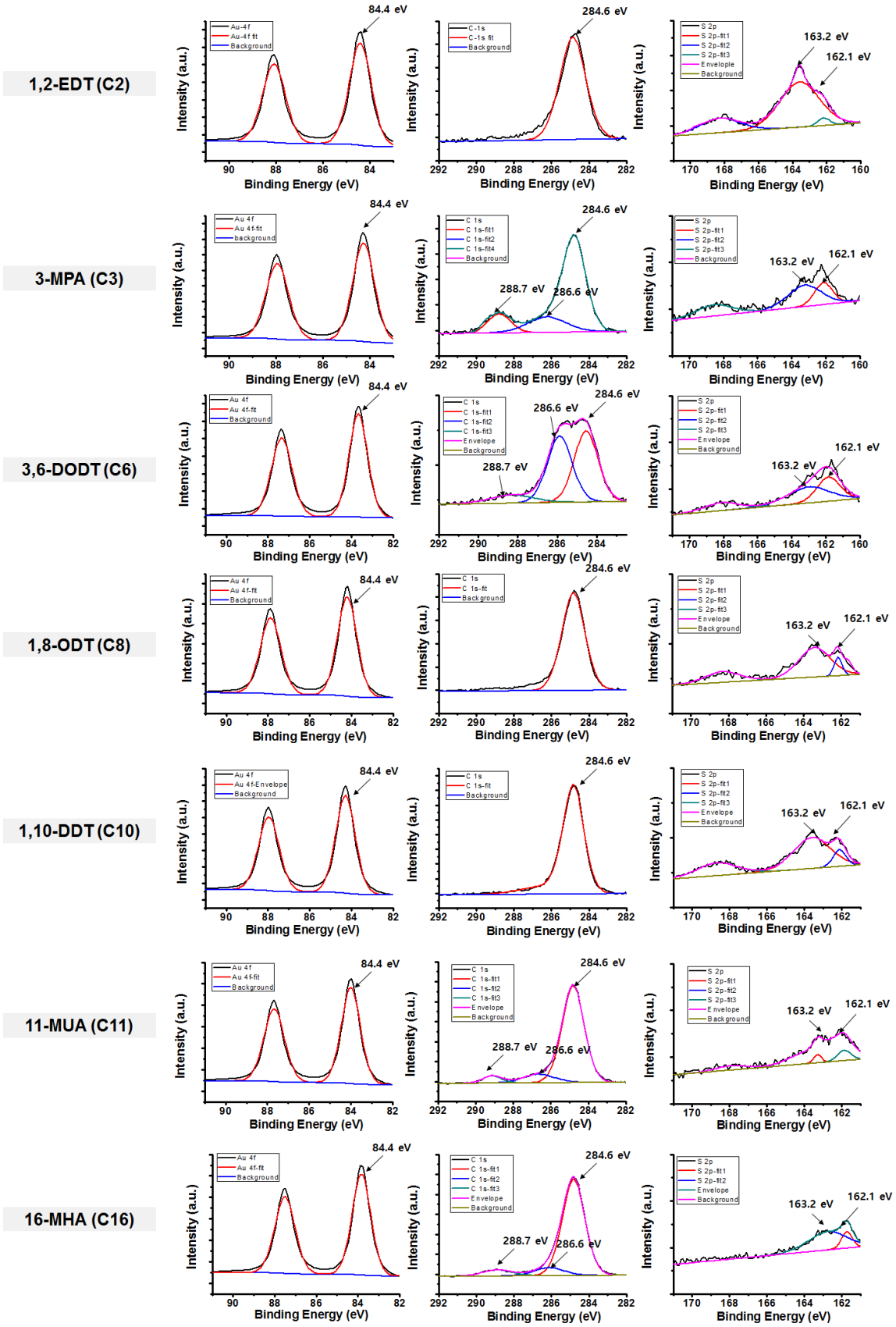

Figure S3. Fitting of Au 4f, C 1s, S 2p XPS data for various chemical functionalizations.

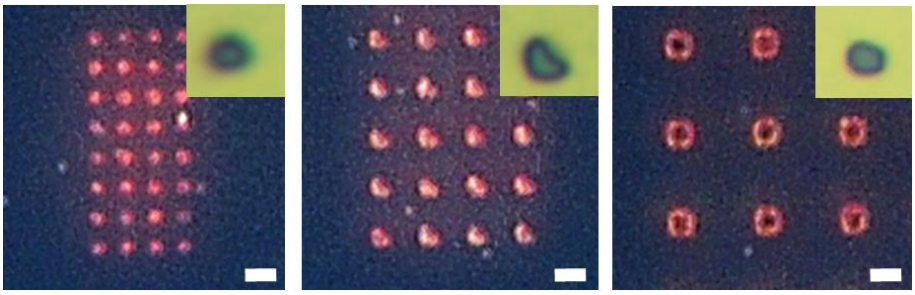

Figure S4 Fabrication of various shapes and sizes of nanostructures on flexible substrate. (Scale bar: 3 μm). The sizes of these nanostructures are 550 nm (circle), 1 μm (half-moon), and 3 μm (circle), respectively (from left to right). The results can support the flexibility of our fabrication process for various applications.

Refractive index sensing

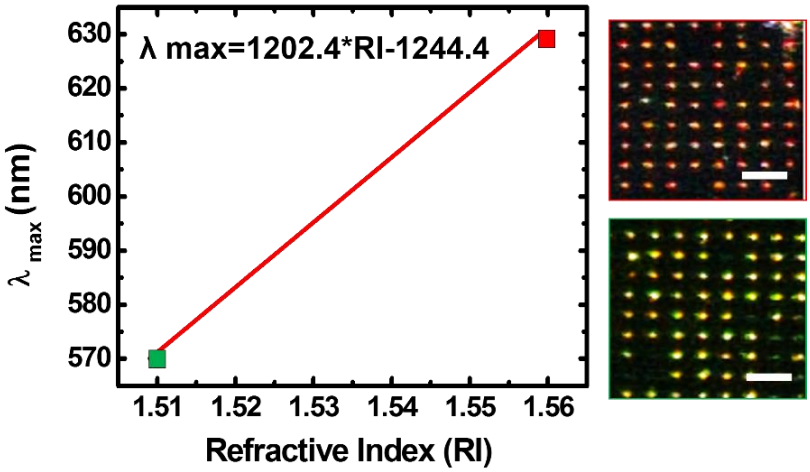

Figure S5. Dark-field microscope images and peak wavelength of the nanostructure array which are functionalized using same thiol terminal group with different body chain: 1, 2-EDT (shown in red box) and 3,6-DODT (shown in green box). (Scale bar: 5 μm) The peak wavelength is changed depending on the refractive index of chemical functionalization used on the plasmonic nanostructures. (Linear regression method)

Plasmon coupling effect

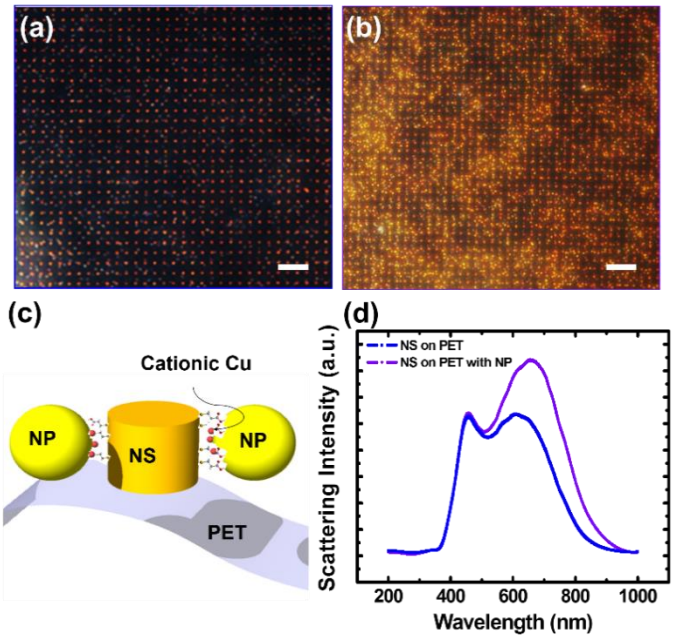

Figure S6. Dark-field images of the transferred nanostructure arrays with (a) functionalization and (b) attachment of nanoparticles with the functional group. (Scale bar: 10 μm) (c) Schematic of plasmon coupling effect between nanoparticles (NP) and nanostructures (NS) on PET. (d) Spectra acquired from NS (shown in (a)) and NS with NP (shown in (b)) indicate the shift of the scattering wavelength and its intensity, thus proving the hybridization of NS with NP.

For a plasmon coupling effect, we have used the printed nanostructure on the flexible substrate, citrate capped nanoparticle, and copper (II) sulfate solution. The printed nanostructure already has a carboxylic acid functional terminal for interacting with the Cu^{2+}. So when the 200 μl solution of Cu^{2+} is dropped on the nanostructure for 1 hour, the Cu^{2+} ions are easily attached to the functionalized nanostructure with electrostatic force. After removing the ions and cleaning the surface with DI water, the 200 μl of 150 nm nanoparticles with a citrate capped functional terminal group are dropped on the printed nanostructure for 1 hour. After that, we have cleaned the surface with DI water and purged with nitrogen gas. So functionalized nanostructure- Cu^{2+}-150 nm nanoparticle assemblies are made, thus showing a red-shifted spectra induced by the plasmon coupling effect.