Supporting Information

Three-Dimensional Assembly of Nanoparticles from Charged Aerosols

Heechul Lee[1], Sukbeom You[1], Peter V. Pikhitsa[1], Junhoi Kim[2], Sunghoon Kwon[2], Chang Gyu Woo[1] and Mansoo Choi [1#]*

[1] National CRI Center for Nano Particle Control, Institute of Advanced Machinery and Design, School of Mechanical and Aerospace Engineering, Seoul National University, Seoul 151-742, Korea.

[*] Present address: Samsung SDI, Gyeonggi-do 446-577, Korea.

[2] School of Electrical Engineering and Computer Science, Seoul National University, Seoul 151- 744, Korea.

Methods

Particle generation and deposition for 3D assembly of nanoparticles

Silver rod (7.0 mm in diameter, 99.99 %), silver foil (2.0 mm in thickness, 99.9 %), silver wool (99.9 %+), copper rod (11.0 mm in diameter, 99.9999 %), copper plate (6.3 mm in thickness, 99.999 %) were purchased from Aldrich. Homemade spark discharge unit and evaporation & condensation equipment were used for generation of charged nanoparticles. A tapered metal tip and a plate with fixed gap distance (~2 mm) are placed in the spark discharge chamber and electric field is applied between the metal electrode tip and the ground plate. At a voltage higher than the critical (about 6 kV), a spark occurs between the tip and plate electrodes, which causes rapid evaporation of electrodes, resulting in the generation of charged nanoparticles and ions. A corona discharger is used to provide N_2 ions for accumulation of ions on PR surface (see Supporting Information Figure S1). In evaporation & condensation method, a nano-DMA (differential mobility analyzer) was used to select monodisperse 10 nm silver nanoparticles. These charged aerosols and ions generated by the corona discharger are injected into a deposition chamber, where photoresist (PR) or SiO_2 pre-patterned Si substrate is located on the electrode with appropriate electric potential. All PR patterns (500 nm rectangular and cross ***patterns***) shown in the main text are prepared by E-beam lithography (JEOL, JBX9300FS) and the height of the PR is 200 nm. Field emission scanning electron microscope (FE-SEM) images of 3D nanoparticle structure were collected with S-4800 (Hitachi, Japan) model operated at 15.0 kV. Morphology and size of nanoparticles were analyzed by transmission electron microscope (JEOL, JEM2100F).

Numerical simulations for particle trajectory and deposition

Numerical simulations for particle trajectory and deposition were performed with our homemade-code by considering Brownian random force, fluid drag force, Coulomb force, image force, and van der Waals force. Electric fields are calculated by finite element based COMSOL 3.2 program. Numerical integration of Langevin's equation is done for determining particle trajectories with variables such as initial velocity, number of elementary charges, moving step size, mean free path, viscosity, Hamaker constants and particle density, by the 4th-order Runge-Kutta method. Electric field calculations were repeated after each ten particle deposition to consider the effect of growing structure.

Raman measurement

SERS substrates were immersed in 1×10^{-3} M ethanol solution of thiophenol (Aldrich) for 3 hours and dried for several minutes. Raman spectra were obtained by a LabRam HR model confocal Raman microscope with LN2 cooled CCD multichannel detector (Jobin-Yvon, France). An argon ion laser with wavelength 514 nm was used as the excitation source and the mean spot size of the laser beam was approximately 700 nm. The laser power radiated to the sample was about 0.02 mW and the acquisition time was 100 sec.

Dark field microscopy

Bright- and dark- field micrographs were obtained with a true-color charge coupled device (CCD) camera (DP72, Olympus) which is directly aligned to conventional reflected light microscope (BX51, Olympus) with a 100 W halogen lamp as a white light illumination source. A 100x dark-field objective lens (NA=0.9) was used for dark-field imaging in combination with a ring-shaped mirror for separating the illumination beam path from the detection beam path. In dark-field imaging mode, only scattered light was collected through the same objective lens and was sent to a CCD camera for imaging.

Supporting Information Figures

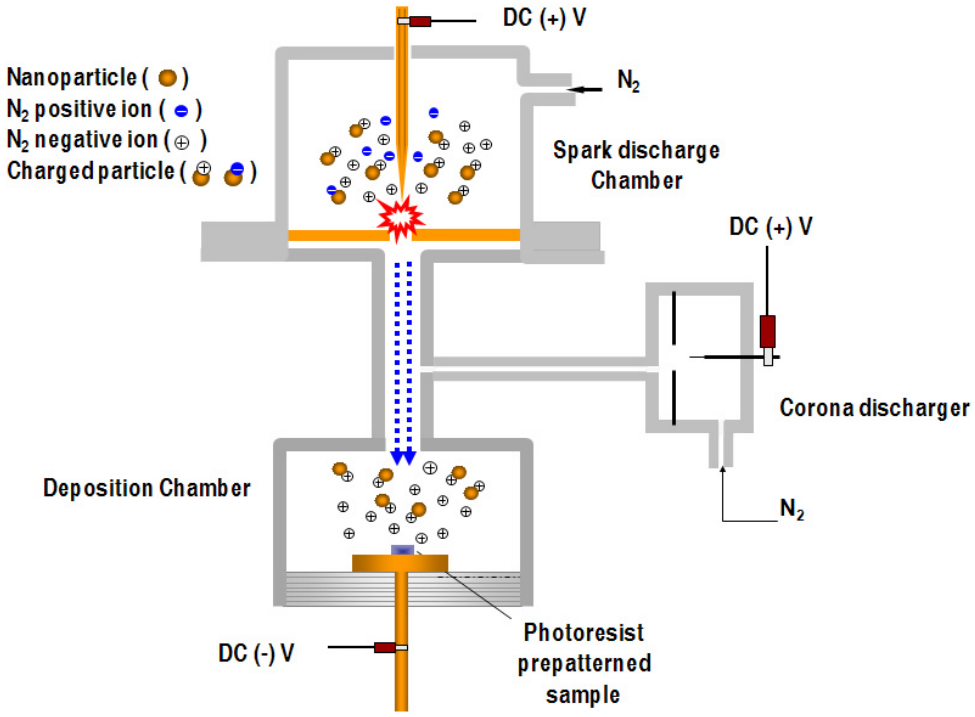

Figure S1. Experimental setup for generation and deposition of charged nanoparticles by spark discharge. Charged nanoparticles and ions having mostly positive charge are generated when the positive voltage is applied to the pin electrode and the plane type electrode is grounded. These are fed into the deposition chamber under N_2 flow rate 4 l min^{-1}. 4 kV negative potential is applied to the substrate to attract ions and charged nanoparticles toward the substrate. Therefore, only positively charged ions and nanoparticles move towards the substrate and a small portion of ions and particles having negative charge cannot be deposited on the substrate. A corona discharger provides N_2 positive ions that are accumulated on the PR surface prior to the deposition. The ions accumulate on the PR surface along the electric field line and form ion induced electrostatic lens. Charged nanoparticles are convergently guided by the lens and placed on the desired position of a substrate.

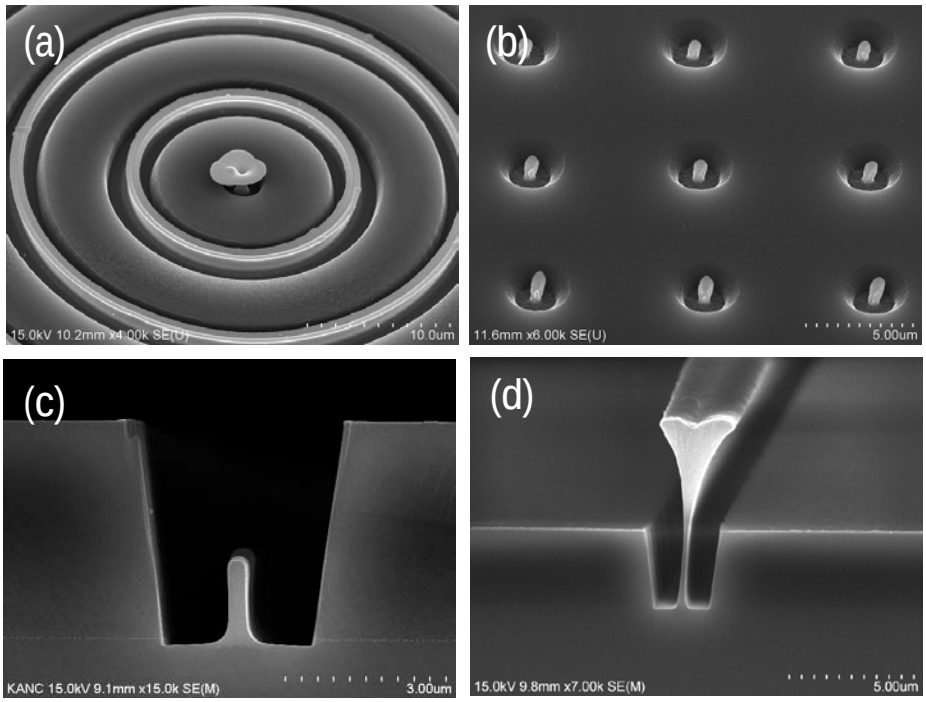

Figure S2. Various 3D nanoparticle structures within micron scale SiO_2 patterns. Extension of 3D pattern of nanoparticles from nanometer scale to micron-scale was successfully achieved through our ion-induced focusing and antenna effects. (a) Circular wall shaped silver microstructures were formed from originally 3-μm-wide curved annular patterns. (b) Pillar-like microstructures were formed within 3-μm circle patterns. (c) High aspect ratio wall shaped copper nanoparticle 3D structure was grown within 3-μm-wide and 4-um-deep microchannel pattern. The aspect ratio of this 3D nanoparticle structure is three times larger than that of original SiO_2 pattern, which means that higher aspect ratio nanoparticle structure can be obtained from relatively low aspect ratio original pattern due to the focusing effect. (d) Fully grown big-head copper mirostructure was formed from originally 3-μm-wide and 4-μm-deep microchannel pattern. This image suggests not only the stability and symmetry of our 3D structure but also the capability of manufacturing high aspect ratio 3D structures consisting of nanoparticles particularly as an ordered array.

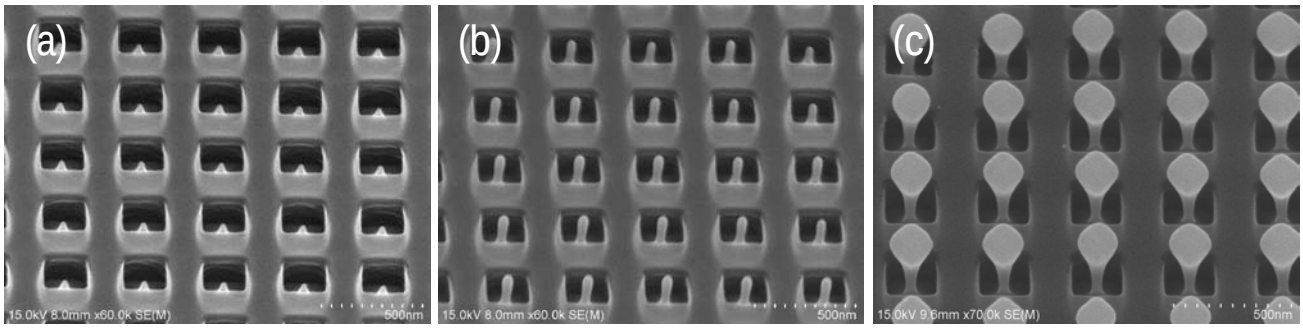

Figure S3. Sequential process of constructing nanoparticle structure within 200 nm wide square PR patterns (PR thickness is 200 nm). Three kinds of nanoparticle structures with same PR patterns were prepared by controlling the deposition time after accumulating N_2 positive ions with 4 l/min for 5 min. (a) Nano-tip arrays of copper nanoparticles were formed after 4 min deposition. (b) Pillar-like structures of copper nanoparticles were formed after 10 min deposition. (c) Matchstick-like structures of copper nanoparticles were formed after 40 min deposition.

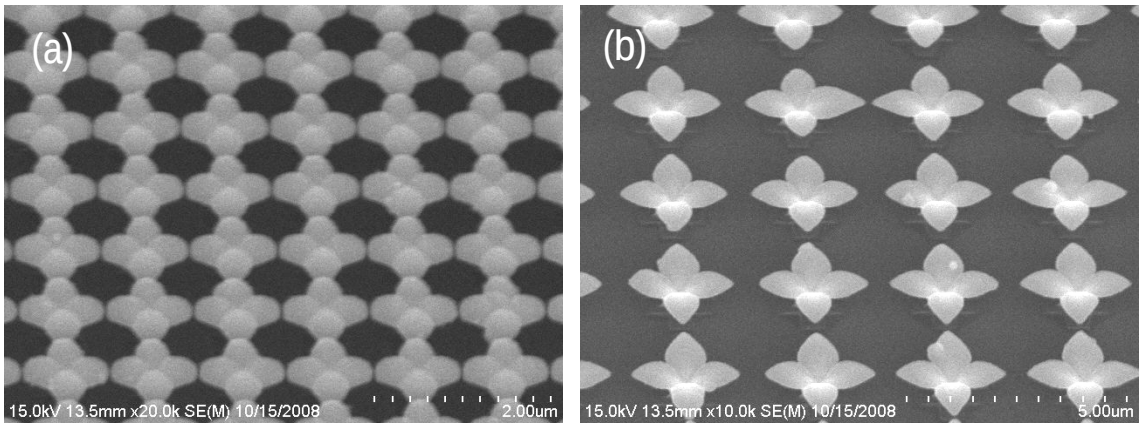

Figure S4. Composite nanoparticle structures consisting of silver and copper nanoparticles. Composite nanoparticle structure arrays were prepared by accumulating silver nanoparticles via spark discharge onto the pre-deposited 3D copper structures and this sequence would be optional. PR layer was removed by dipping a sample into the 1-butanone solution for several minutes. (a) Four-leaf clover-like composite 3D structures from originally square PR patterns with one side of 500 nm. (b) Flower-like composite 3D structures from originally cross PR patterns with one side of 500 nm.

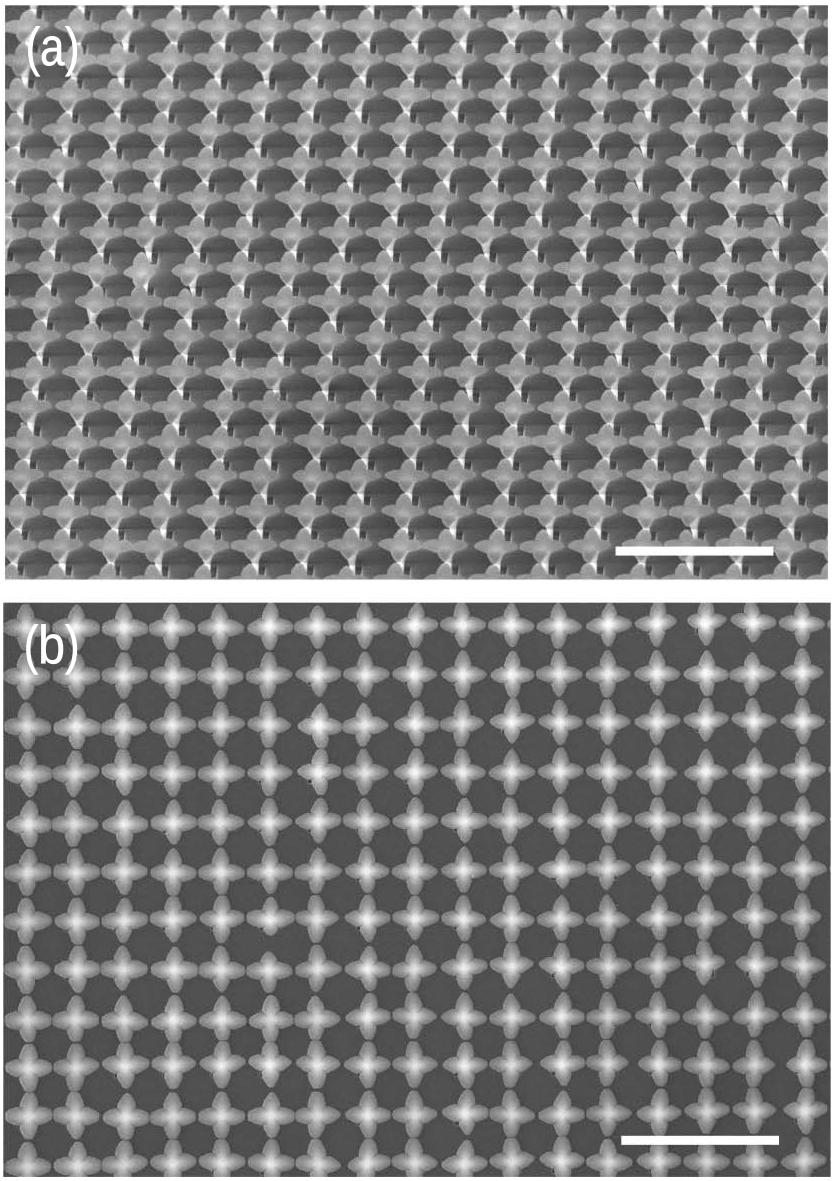

Figure S5. Array of four leaf clover like 3D nanoparticle structures in large area. Four-leaf clover-like nanoparticle structures are formed very uniformly within 500 nm square patterns in large area (PR spacing is 1 μm, which is twice larger than that of Fig 2(a)-sample). (a) 45^{o} tilted view image. (b) Top view image. All scale bars correspond to 5 μm.

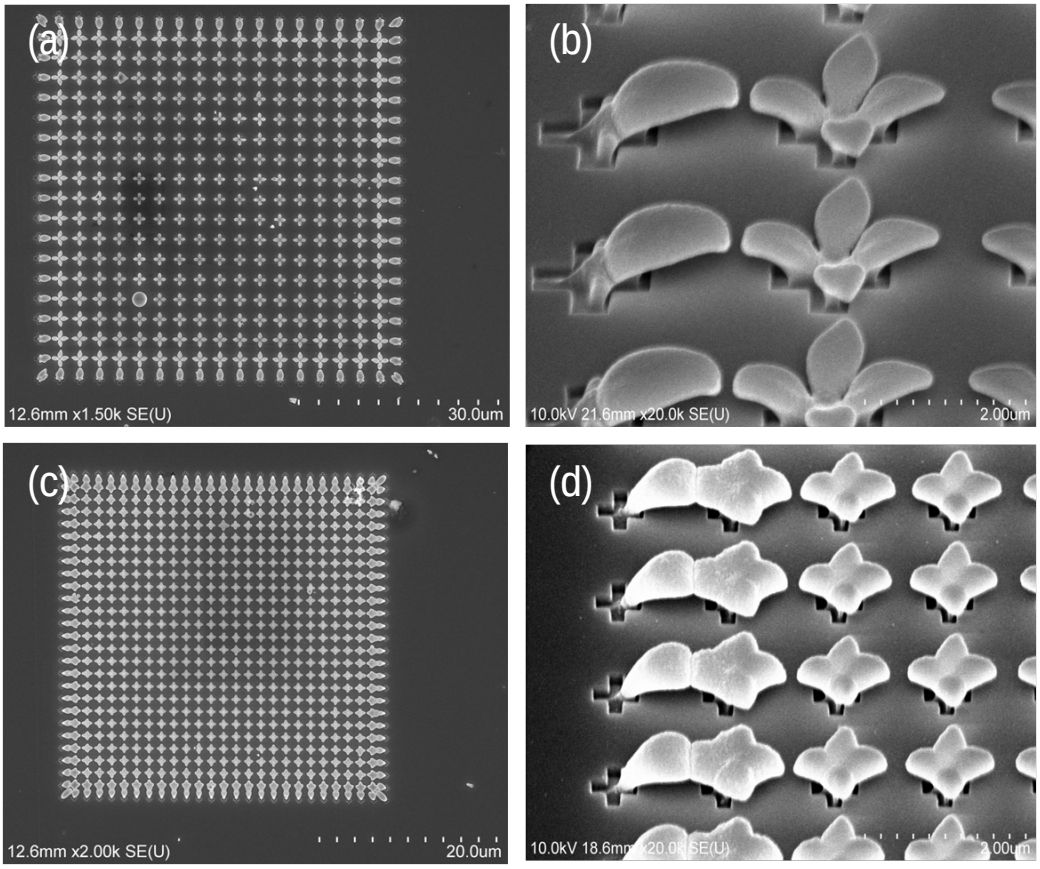

Figure S6. Top view and tilted view images of 3D flower shaped nanoparticle structures on the (a), (b) 500-nm-wide and (c), (d) 200-nm-wide cross PR prepatterned Si substrate

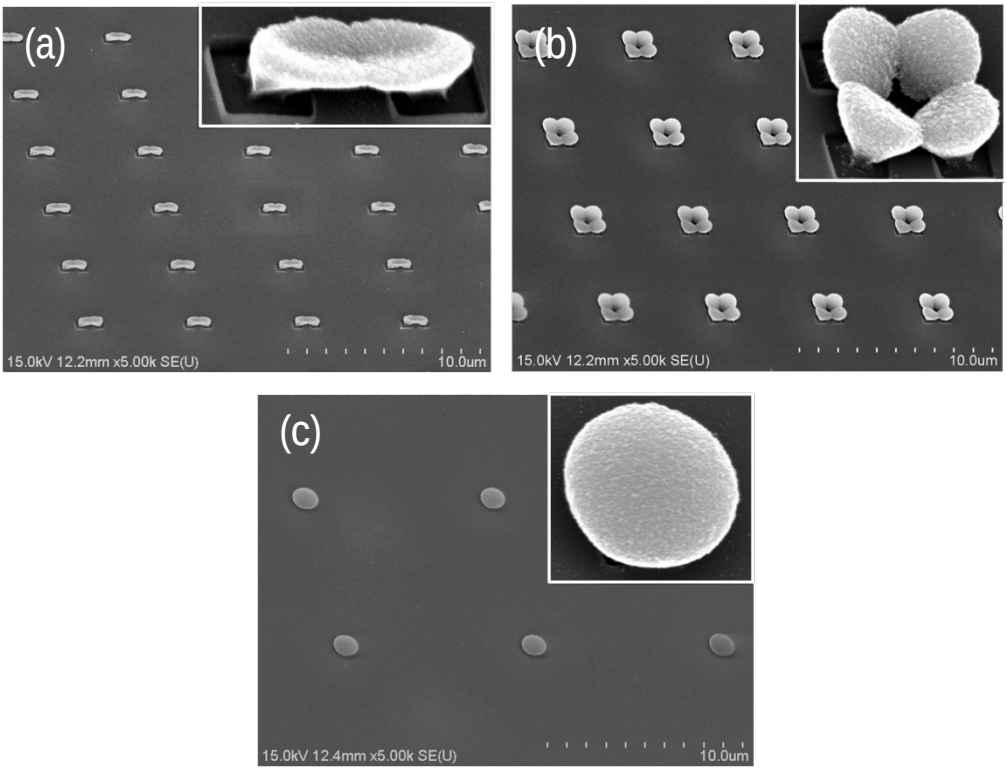

Figure S7. Asymmetric 3D nanoparticle structures and symmetric round shape 3D nanoparticle structure depending on pattern arrangement. (a) "Micro-table- like 3D nanoparticle structures" obtained from two adjacent equal square patterns. (b) Flower structures having a central hole from four proximal square patterns. (c) Symmetric round shape 3D nanoparticle structure from isolated square PR patterns.

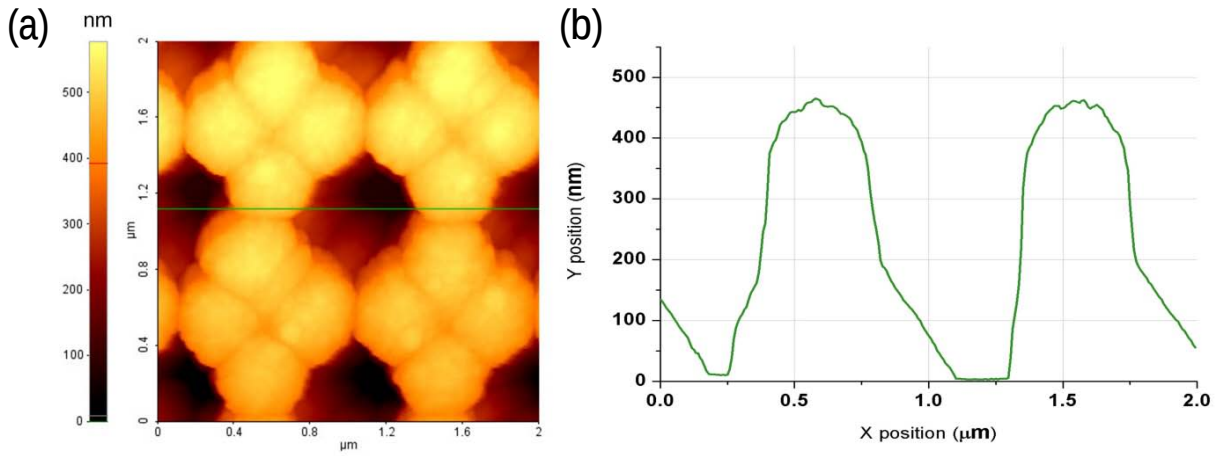

Figure S8. AFM image of four leaf clover-like 3D nanoparticle structure. (a) AFM image. (b) topography of nanoparticle structure near the edge of clovers along the line shown in (a) Height from the bottom Si surface is about 470 nm.

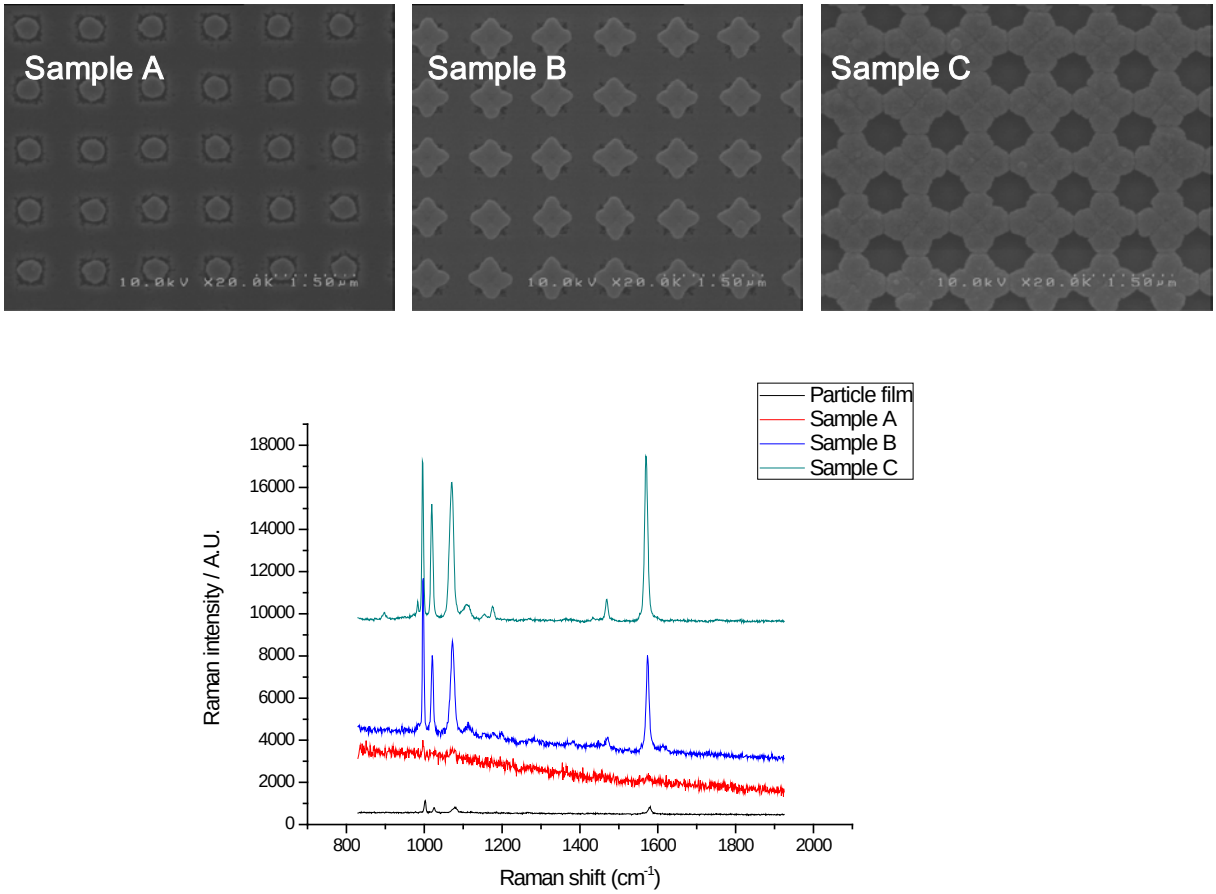

Figure S9. SEM images and corresponding SERS spectra of thiophenol on gold-film covered 3D copper patterns per unit area of copper coverage. The laser at 632 nm was used for excitation. The spectra were shifted for clarity. Gold film on silicon without copper particles gives no SERS signal and was excluded from the area. The sample of gold-covered copper nanoparticles uniformly deposited on silicon substrate was a reference "flat" sample with 100% coverage ("Particle film"). Sample A has round flat features and thus shows no 3D geometry SERS enhancement (thiphenol peaks from Sample A and Particle film are nearly identical save for the low signal to noise ratio because of low copper coverage in Sample A). One can notice a fine structure in the sample C spectrum (of the same quality as for patterns covered with silver particles in Fig. 5) made clearly visible due to additional 3D geometry SERS enhancement of 28 times. It is instructive to compare the quality of the sample C SERS spectrum with high-quality analogs from gold-covered micro-patterned Si surface with pyramidal pits [Ohta, N.;

Yagi, I. *J. Phys. Chem. C*, **2008**, 112, 17603–17610]. One can make sure that our 3D geometry of the structure makes the SERS spectra outperform the planar analogs in quality.

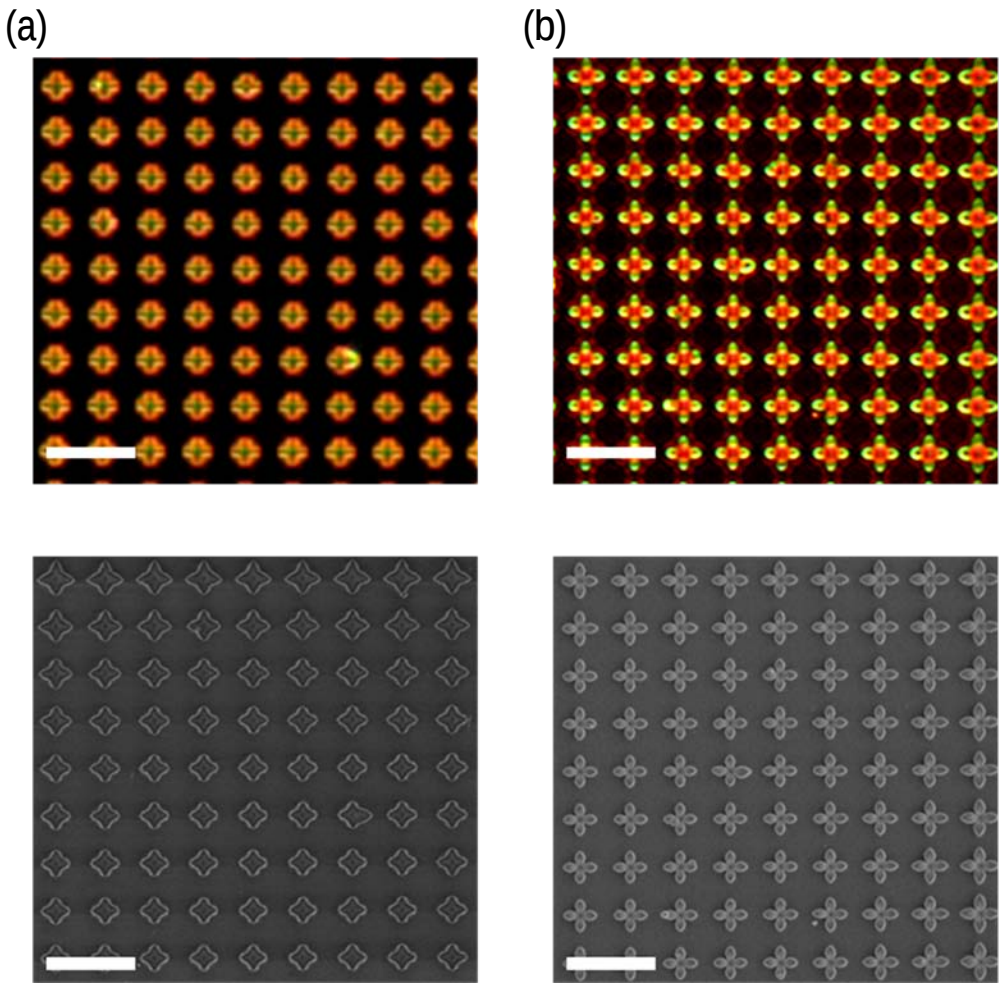

Figure S10. Dark field scattering image (Top) and SEM image (Bottom) of (a) silver nanoparticle covered and (b) gold-film covered 3D copper nanoparticle structure arrays. The scale bar is 5 μm.