Laser Metallurgy Route for Batch Preparation of mm-scale 3D Silver/Graphite Hetero Nanoclusters in Air

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Experimental Procedures

Chemical Reagents. Silver oxide (II) (Ag_2O, 99%), benzene-1,3-dicarboxylic acid (H_2bdc, $C_6H_6O_4$, 99%), pyrazine (py, C_5H_5N, 99%), malachite green (MG, $C_{23}H_{25}ClN_2$, analytical grade) were all purchased from Aladdin. Methanol absolute (CH_4O, 99%) were offered by Sinopharm Chemical Reagent Co., Ltd. Methamphetamine (MATM, $C_{10}H_{15}N{\cdot}HCl$, CP, 0.5 g) were provided by the Wuhan Public Security Bureau Anti-Drug Detachment. All chemicals and solvents used in the syntheses were of analytical grade and used without further purification.

The synthesis of [Ag_2(pz)(bdc)·H_2O]$_n$ (1). A mixture of Ag_2O (57.9 mg, 0.25 mmol), H_2bdc (83.1 mg, 0.5 mmol), pz (40.0 mg, 0.5 mmol) and 0.5 mL $NH_3{\cdot}H_2O$ (25%) was treated in CH_3OH-H_2O (6 mL, v : v = 1:1) under ultrasonic irradiation at ambient temperature. The resultant solution was allowed to evaporate slowly in darkness at ambient temperature for several days to give colourless rod-like crystals of 1 (yield: 80%, based on Ag). They were washed with a small volume of cold CH_3OH and dried in air. The phase purity of this Ag^I-based coordination network was confirmed by powder X-ray diffraction (PXRD), the pattern of which matched well with the simulated pattern based on the single crystal structure of **1** in the reported work.

The synthesis of Ag/graphite nanostructure in the glass capillary. The graphite-protected Ag nanostructure were prepared through nano-LaMP method. Firstly, the Ag^I-based coordination network were dispersed in the cold CH_3OH, then the suspensions were filled into the caplillary with a diameter of 0.3 mm through an injection syringe. Secondly, graphite protected metallic Ag was produced by direct laser scribing on the solid AgI-based coordination network powders, which convert the metallic-based coordination network to form Ag nanoparticles covered by thin protective graphite outer layers. These Ag nanoparticles were deposited and filled as a thin film of continuous 3D architecture in the capillary. The line width of the laser beam can be set to between 55 to 380 μm according to the focus length.

The synthesis of Ag/graphite nanostructure on the top glass. The Ag^I-based coordination network powder was packed through gradually filling a circular mold surrounded by a metal foil between two glass slides. Metallic Ag was produced by direct laser scribing on the solid AgI-based coordination network powders, which convert the coordination network to form Ag nanoparticles covered by thin protective graphite outer layers. These Ag nanoparticles were deposited as a thin film of continuous 3D architecture on the top glass. The line width of the laser beam can be set to between 55 to 380 μm according to the focus length

The SERS measurements. All the chemical reagents related to these experiments were used directly without any other purification. Firstly, the 1×10^{-3} mol/L mother solution of internal standard molecule Malachite Green (MG) used in the preparation of Raman probes was prepared by dissolving 36.4 mg of MG solid into 100 mL deionized water. and then diluted step by step to prepare a series of graded concentration solution. The standard solutions with different concentrations were obtained: 10 μM, 5 μM, 1 μM, 500 nM, 100 nM, 50 nM, 10 nM, 5 nM. The various concentrations of MG solutions were injected into the graphite-protected Ag nanoparticle three-dimensional architectures filled in the capillary. Then we focused the laser on the middle of capillary to take the SERS measurements (conducted with a Renishaw Raman microspectromenter (Smart 4.0)) with a 532 nm excitation laser and a 20L× objective.

10 mg methamphetamine was solved by 10 mL deionized water to obtain the 1000 ppm mother solution of MATM, and then diluted also with deionized water step by step to obtain a series of standard samples in other concentrations: 1000 ppm, 500 ppm, 100 ppm, 50 ppm, 10 ppm, 5 ppm, 1 ppm. Then, the SERS measurements of MATM absorbed in the graphite-protected Ag nanoparticles three-dimensional architectures.

Characterization. All the extinction spectra were measured by a Varian UV–vis-near infrared spectrometer (UV-2550, Shimadzu, Japan). And the SEM images were taken by field-emission scanning microscopy (FE-SEM, SIGMA, Germany). The TEM images came from transmission electron microscope (TEM, JEOL JEM-2010 microscope, Japan) operated at 120 kV. Raman measurements were collected from a Raman microscope (in Via-Plus, Renishaw, Germany) equipped with a 632.8 nm excitation laser and a 20L× objective.

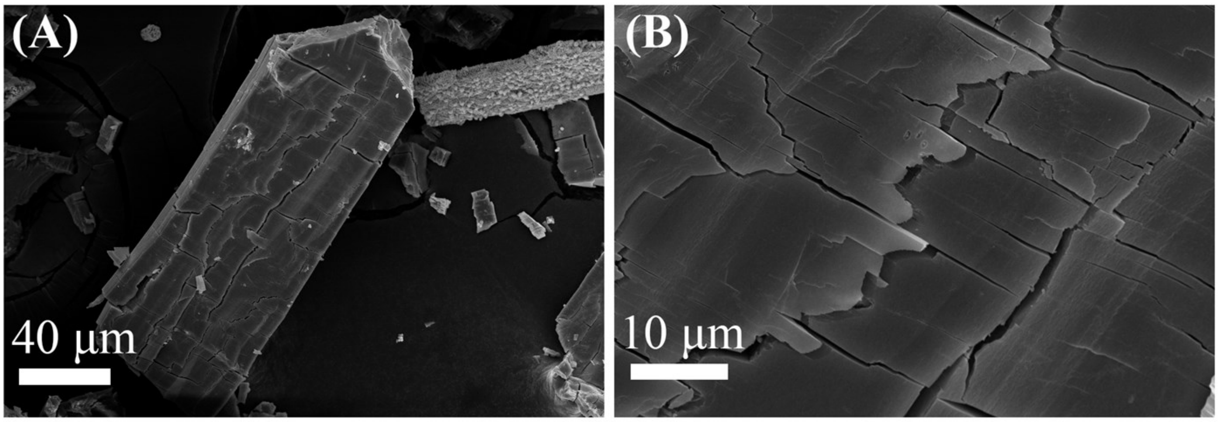

Figure S1. The SEM image of Ag^{I}-based coordination network, namely $[Ag_2(pz)(bdc)\cdot H_2O]_n$ (1).

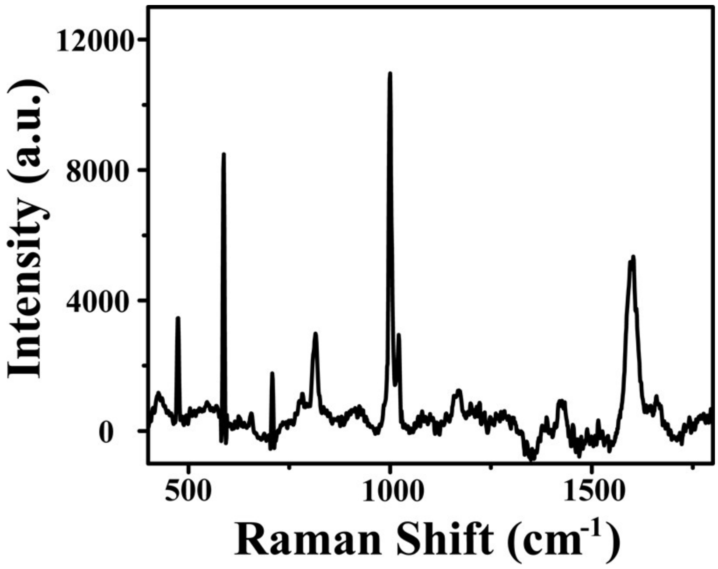

Figure S2. The Raman spectrum of Ag^{I}-based coordination network, namely $[Ag_2(pz)(bdc)\cdot H_2O]_n$ (1).

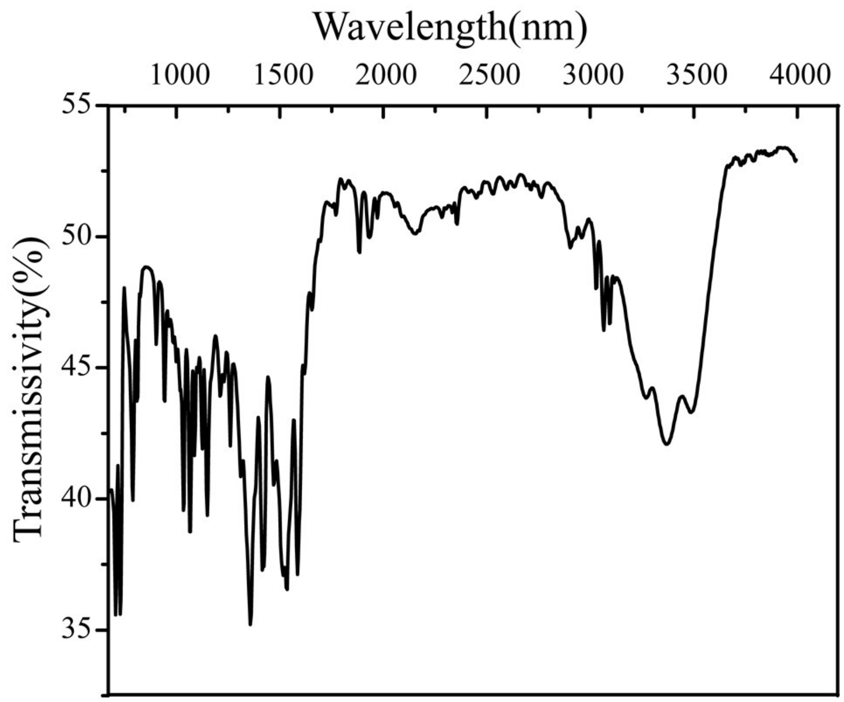

Figure S3. IR spectra of $[Ag_2(pz)(bdc)\cdot H_2O]_n$ at room temperature.

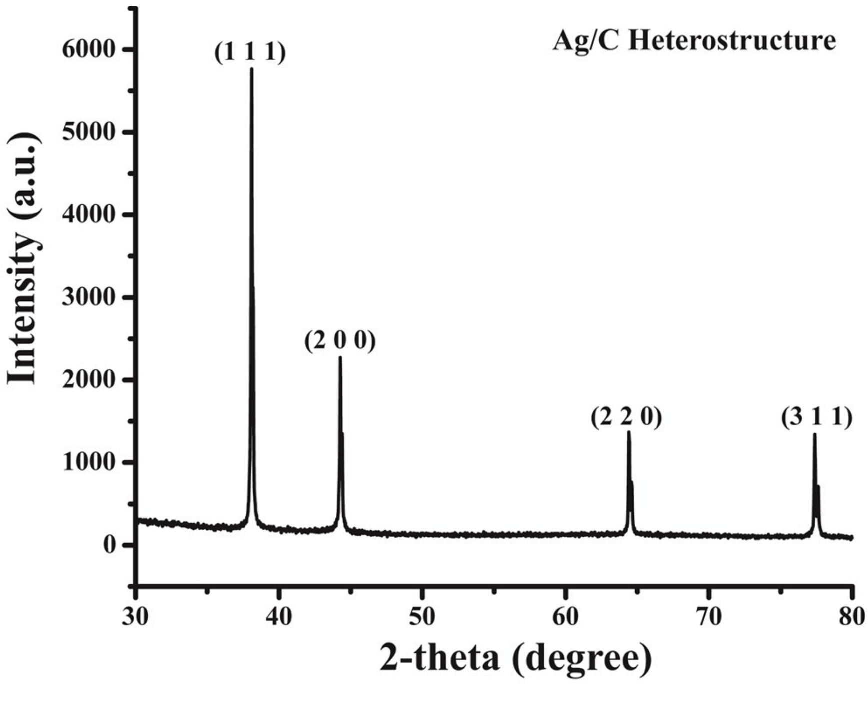

Figure S4. The XRD pattern of mm-scale 3D silver/graphite hetero-nanoclusters.

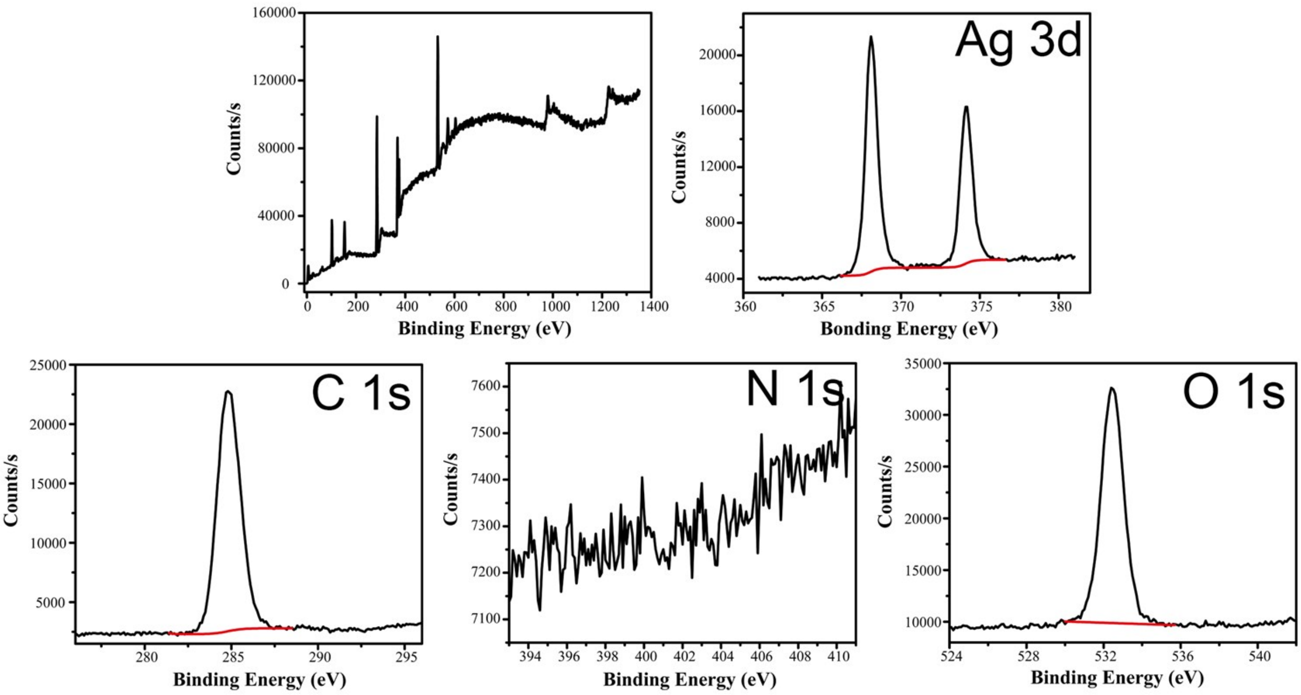

Figure S5. The XPS pattern of mm-scale 3D silver/graphite hetero-nanoclusters.

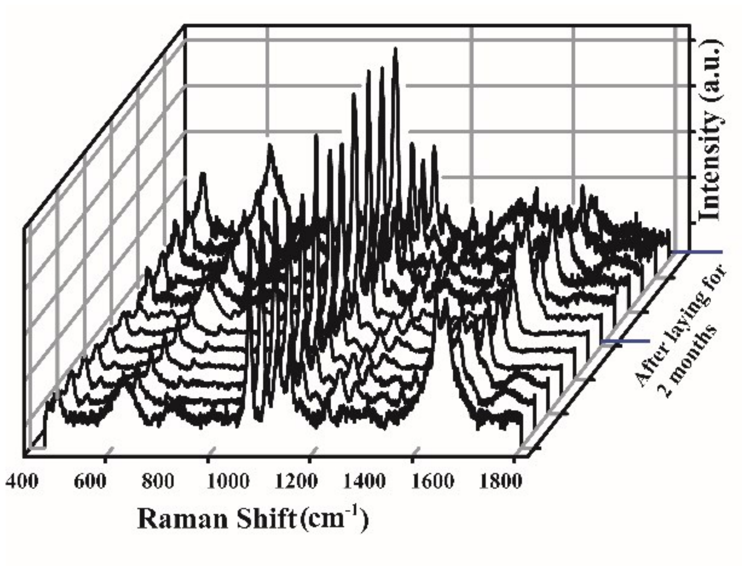

Figure S6. The SERS spectra of MG absorbed on mm-scale 3D silver/graphite hetero-nanoclusters by laying for 2 months

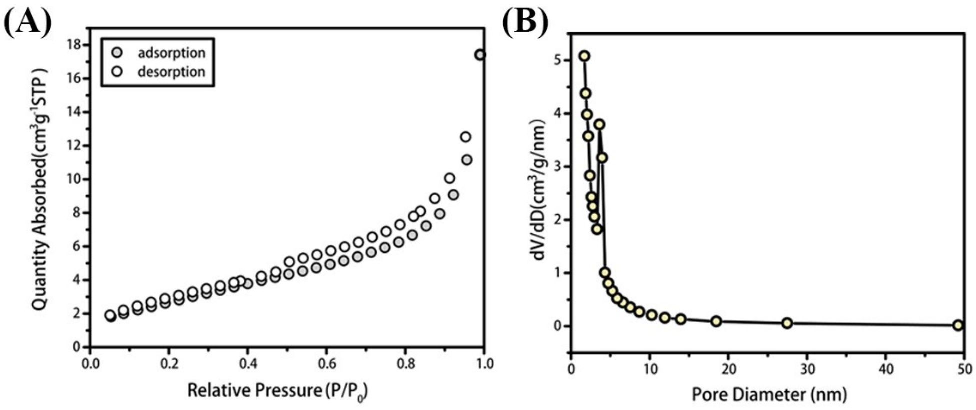

Figure S7. The BET absorption test of mm-scale 3D silver/graphite hetero-nanoclusters.

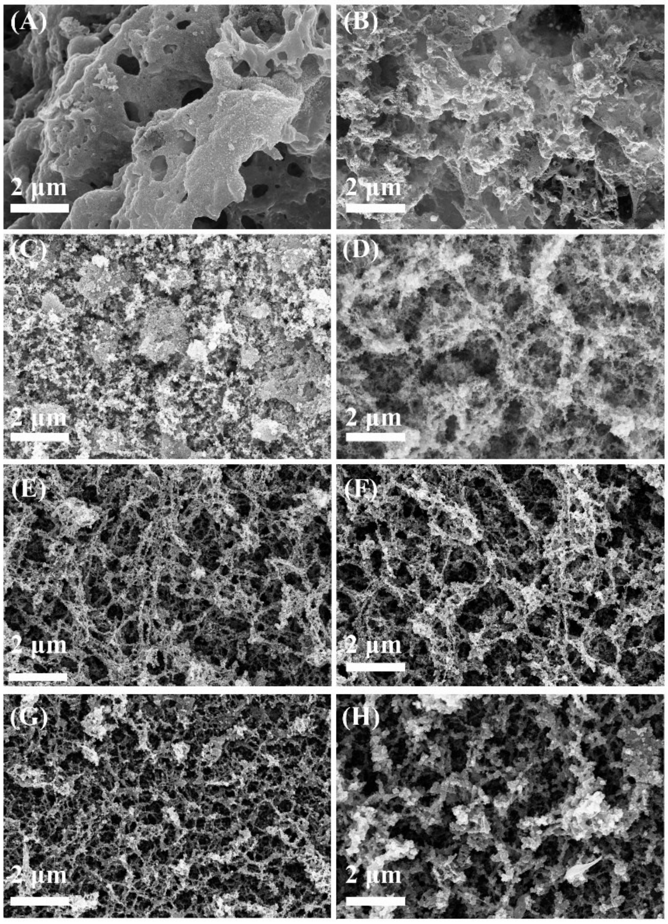

Figure S8. The SEM images of mm-scale 3D silver/graphite hetero-nanoclusters in 20 W (A), 30 W (B), 40 W (C), 50 W (D), 60 W (E), 70 W (F), 80 W (G), and 90 W (H).

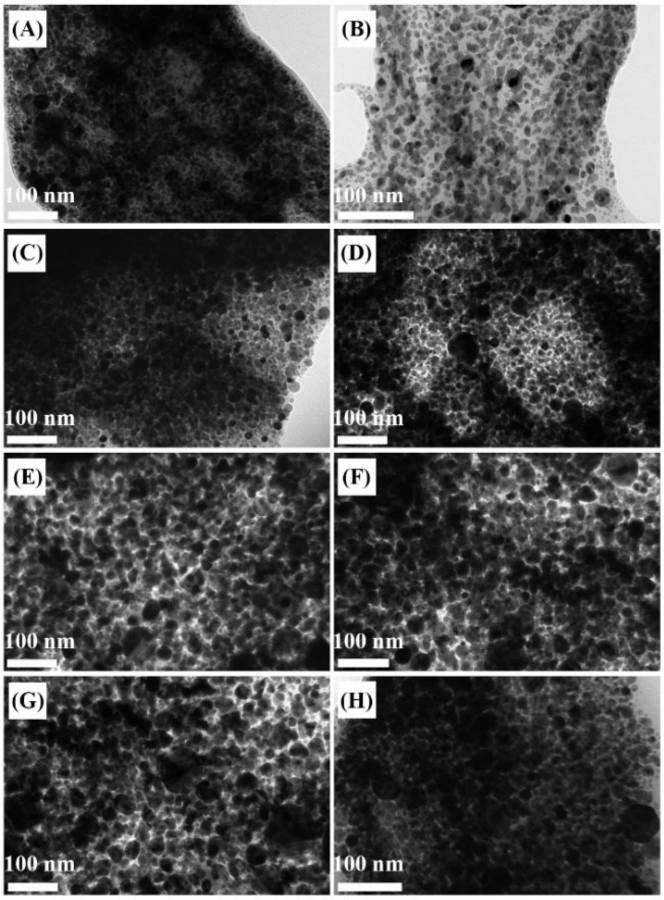

Figure S9. The TEM images of mm-scale 3D silver/graphite hetero-nanoclusters in 20 W (A), 30 W (B), 40 W (C), 50 W (D), 60 W (E), 70 W (F), 80 W (G), and 90 W (H).

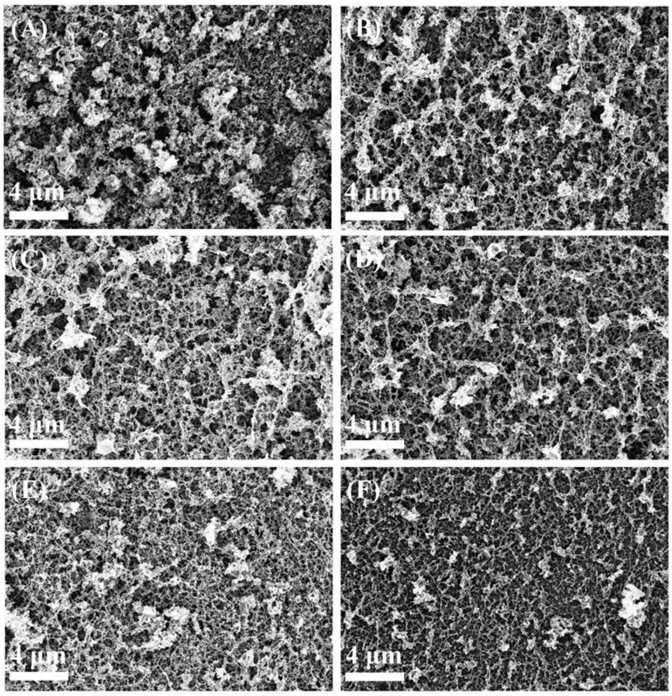

Figure S10. The SEM images of mm-scale 3D silver/graphite hetero-nanoclusters prepared in 40 mm/s (A), 50 mm/s (B), 60 mm/s (C), 70 mm/s (D), 80 mm/s (E, and 90 mm/s (F). (Laser power: 60 W)

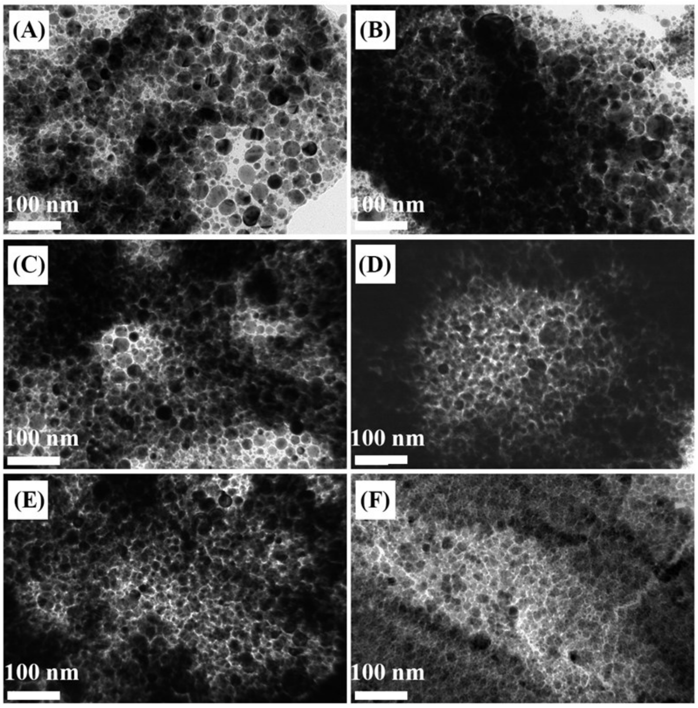

Figure S11. The TEM images of mm-scale 3D silver/graphite hetero-nanoclusters prepared in 40 mm/s (A), 50 mm/s (B), 60 mm/s (C), 70 mm/s (D), 80 mm/s (E, and 90 mm/s (F). (Laser power: 60 W)

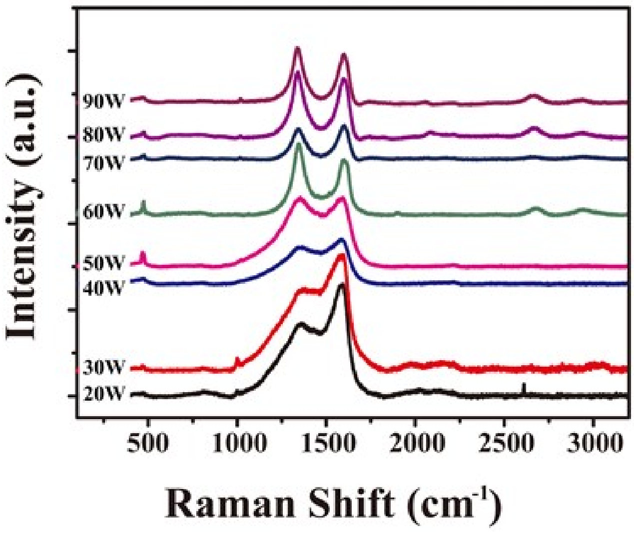

Figure S12. The Raman spectra of mm-scale 3D silver/graphite hetero-nanoclusters prepared in 20 W, 30 W, 40 W, 50 W, 60 W, 70 W, 80W, and 90 W.

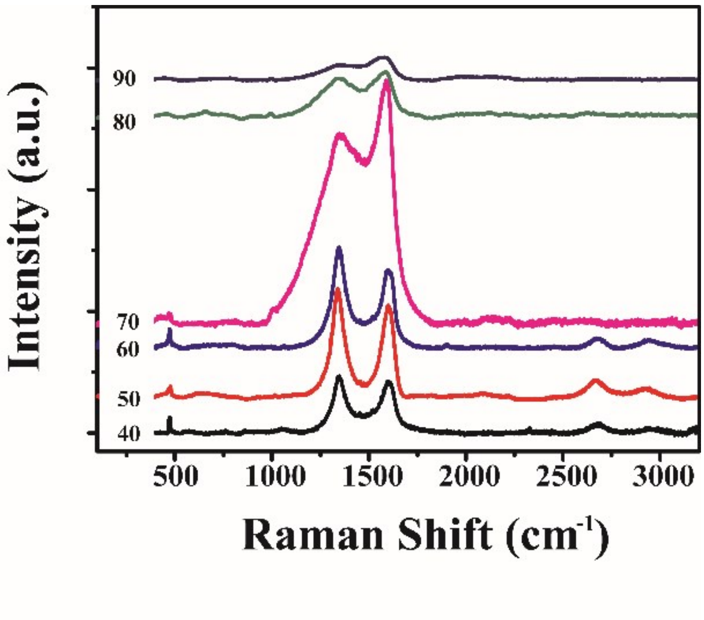

Figure S13. The Raman spectra of mm-scale 3D silver/graphite hetero-nanoclusters prepared in 40 mm/s, 50 mm/s, 60 mm/s, 70 mm/s, 80 mm/s, and 90 mm/s. (Laser Power: 60 W)

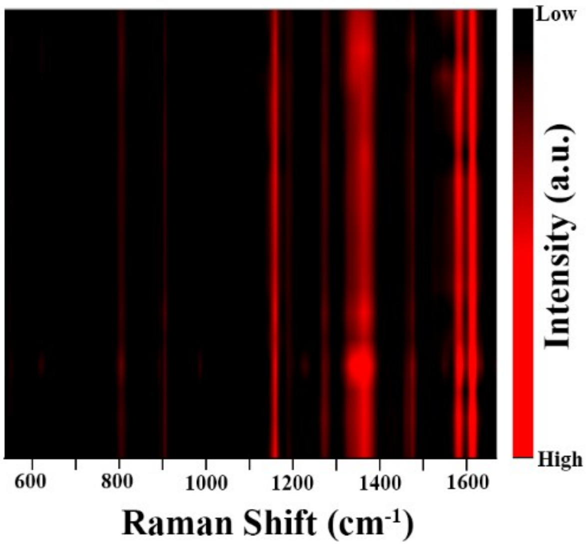

Figure S14. The Raman spectra of MG-functional mm-scale 3D silver/graphite hetero-nanoclusters in different batches.

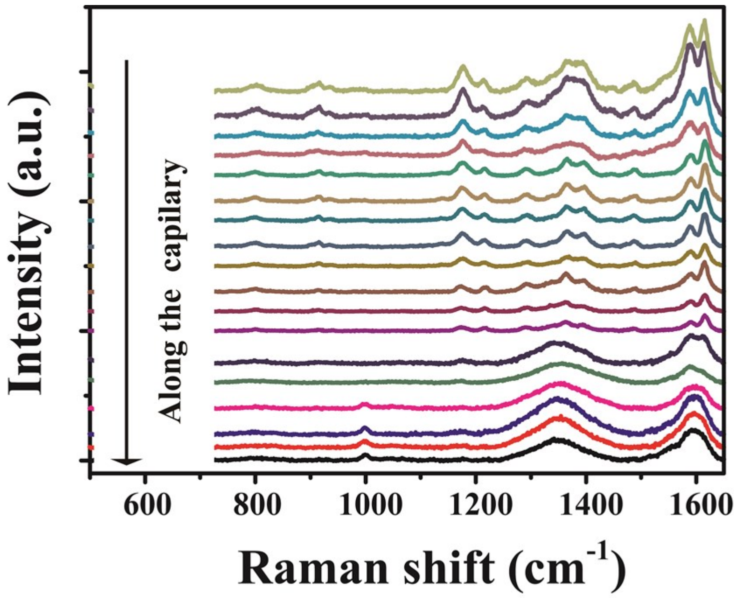

Figure S15. The SERS spectra of mm-scale 3D silver/graphite hetero-nanoclusters along the capillary.

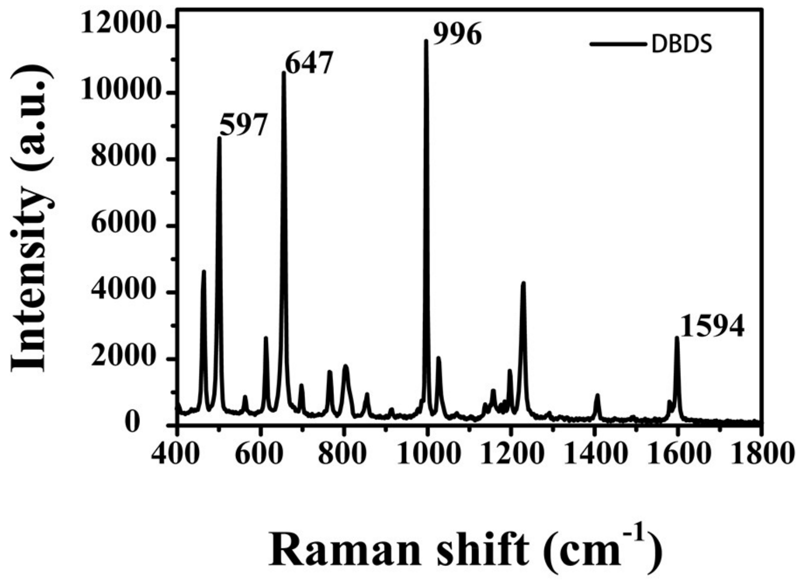

Figure S16. The Raman spectra of DBDS powder

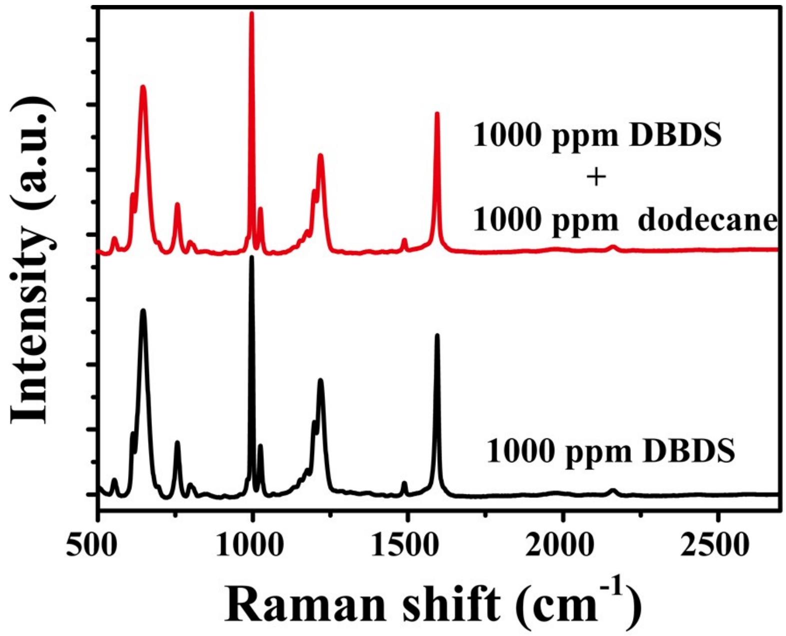

Figure S17. The Raman spectra of 1000 ppm DBDS solution and the equal concentration of mixed solution of DBDS and dodecane.