Supporting Information

3D Nanoporous Plasmonic Chips for Extremely-Sensitive NO_2 Detection

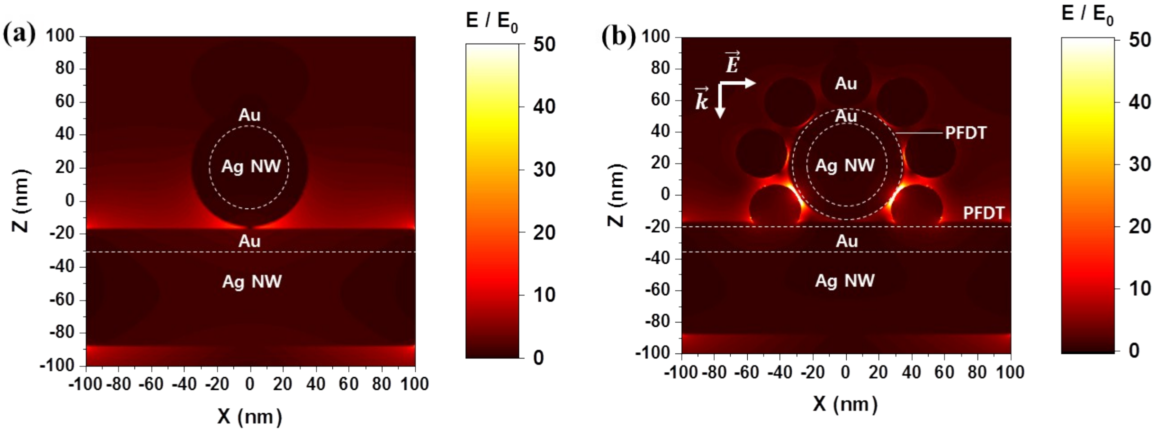

Fig. S1. Finite-difference time-domain (FDTD) simulation results of electric field intensity distribution of (a) 3D stacks of Au–Ag bimetallic nanowire (NW) structures with Au thickness of 15 nm, and (b) 3D stacks of Au–Ag bimetallic NW structures whose surfaces are decorated by spherical Au NPs at the wavelength of λ=785 nm. Since the local field enhancement is inversely proportional to gap size between metal nanostructures, the 3D structures provide a high density of hotspots and a large Au surface for effective adsorption of NO_2 gas molecules, as shown in (b).

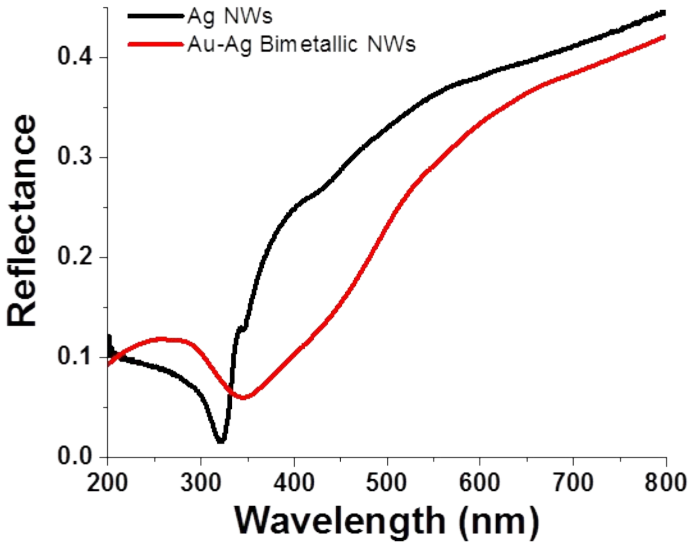

Fig. S2. Reflectance spectra of the 3D Ag NW and Au–Ag bimetallic NW structures. The 3D Ag NW structures revealed a distinct reflectance dip near 320 nm, corresponding to the interband transition (～3.8 eV) of Ag. As the Au deposition layer was formed on the Ag NW structures, the interband transition of the 3D Au–Ag bimetallic NW structures was red-shifted to 350 nm. The reflectance intensity of the 3D Au–Ag NW structures in the 600–800 nm range was found to be the lower than that of 3D Ag NW structures, suggesting that the optical properties were improved compared to those of the 3D Ag NW structures.

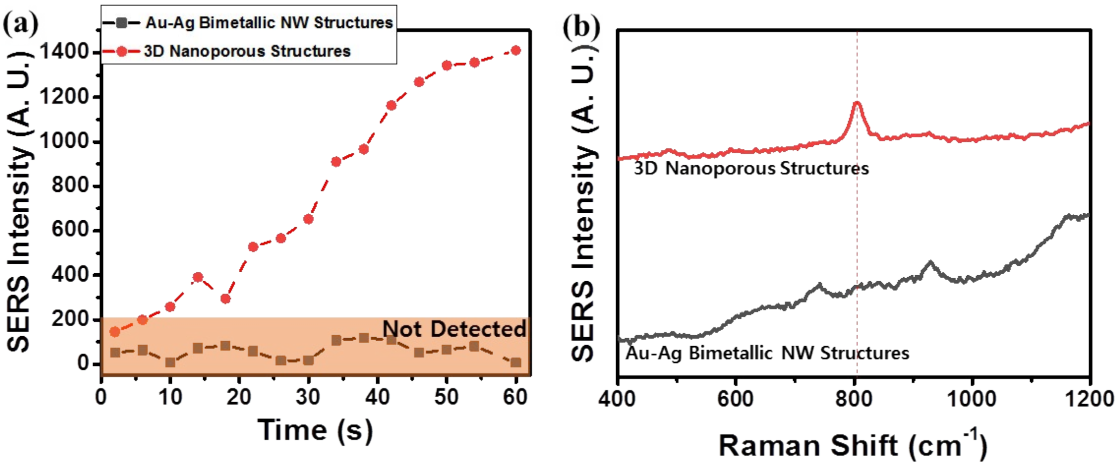

Fig. S3. (a) SERS intensity changes at 810 cm^{-1} as a function of flowing time at NO_2 concentration of 0.1 ppm on Au–Ag bimetallic NW structures and Au–Ag bimetallic NW structures with Au NPs (i.e., 3D nanoporous chip). (b) SERS spectra of NO_2, after 60 s exposure on each 3D SERS substrate.

<Calculation of the SERS enhancement factor (E.F) of Au−Ag bimetallic NW structures and 3D nanoporous SERS substrate using benzenethiol (BT) molecules>

The enhancement factor was determined by the following Equation.

$$E.F = \frac{I_{SERS}\ N_{Raman}}{I_{Raman}\ N_{SERS}}$$

In this equation, N = C•V•NA/S, where C, V, NA, and S represent the concentration (2 mM for SERS measurement and 100% for normal Raman measurement) of BT solution, the volume of the BT solution (10 μL) dropped, Avogadro constant and the area of the BT molecules covered (5×5 mm^2 for SERS and 22×22 mm^2 for normal Raman measurement), respectively. Both substrates were dried in the air. The foregoing equation thus becomes as following Equation.

$$E.F = \frac{I_{SERS}\, S_{SERS} V_{Ref} C_{Ref}}{I_{Ref}\, S_{Ref} V_{SERS} C_{SERS}}$$

From this equation, the SERS EF was determined to be 1.9×10^6 for the Au−Ag bimetallic NWs substrate. The optimized nanoporous SERS substrate showed an improved SERS EF of 4.0×10^6 at 1008 cm^{-1} (red solid line in Fig. S4).

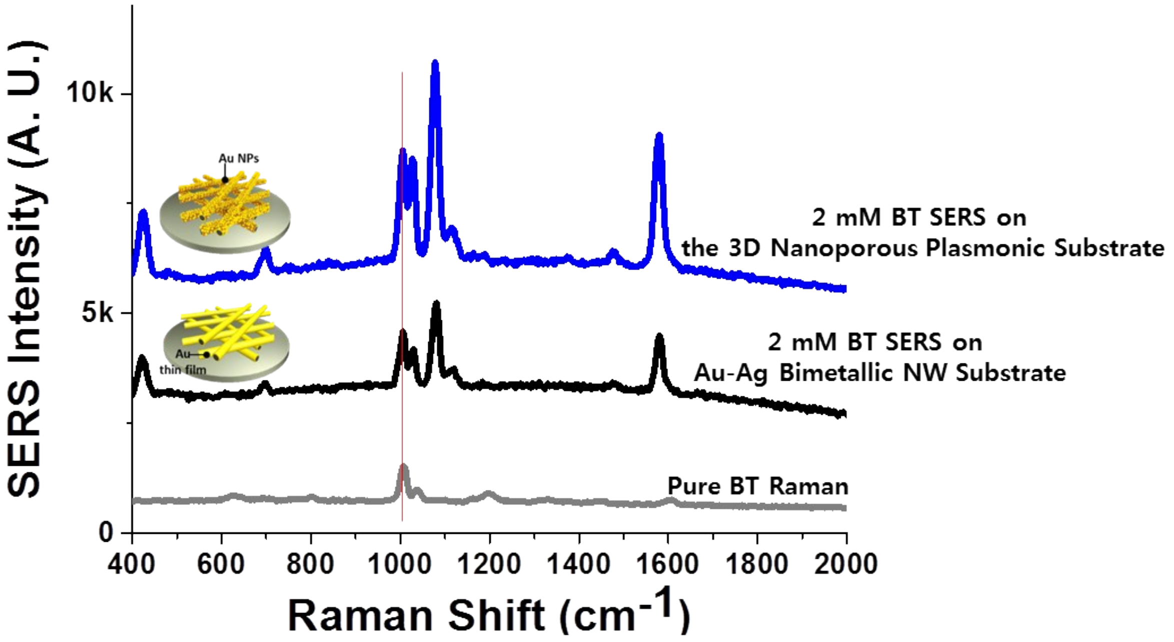

Fig. S4. Raman signal comparison between Au-Ag bimetallic NWs and 30 nm-thick Au layer on the Au-Ag bimetallic NWs and a neat BT Raman measurement for SERS enhancement factor calculation. The laser exposure time was 2 s for each measurement.