Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Analyte-concentrating 3D hybrid plasmonic nanostructures for use in highly sensitive chemical sensors

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This supplementary information includes:

Enhancement Factor Calculation

Supplementary Figures (Figure S1-S3)

Supplementary Videos (Video 1-3)

- Enhancement Factor Calculation

The average enhancement factor (EF) of the SERS substrate was defined as

$$EF = (I_{SERS}/I_{Raman}) \times (N_{Raman}/N_{SERS})$$

where I_{SERS} is the SERS intensity of the probe molecules (in our case, benzenethiol (BT) molecules), I_{Raman} is the normal Raman intensity of BT, N_{SERS} is the number of BT molecules adsorbed onto the SERS substrate, and N_{Raman} is the number of BT molecules present in the Raman measurements.

- I_{SERS} and I_{Raman} Calculation

Based on the Raman intensities at 998 cm^{-1} and 1015 cm^{-1}, I_{SERS}/I_{Raman} are 6.6×10^2 and 1.7×10^3, respectively.

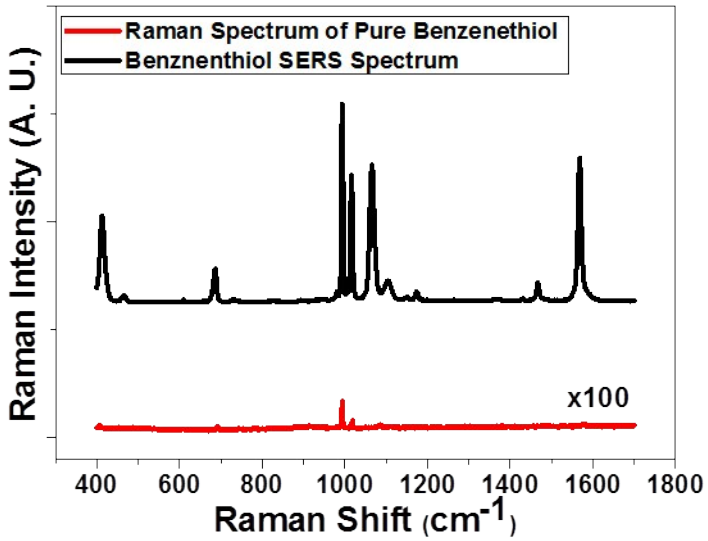

Fig. S1 SERS spectrum measured from the benzenethiol monolayer-treated 3D Ag nanostructures (black line), and the normal Raman spectrum obtained from the pure benzenethiol solution (red line).

- N_{SERS} and N_{Raman} Calculation

We used a 50x objective lens (NA = 0.5) to conduct the Raman measurements. The detection beam diameter was 1.54 μm, and the illumination area was 1.86 μm^2. The packing density of BT molecules across the Ag surface was 6.8×10^{14} cm^{-2}.[1] The areal density of Ag NPs with oblate ellipsoid shapes was 330 μm^{-2}.[2] The surface area of the Ag NPs was calculated as follows. For simple calculation, the Ag NPs assumed to be half-spheres and to be 50 nm in diameter. Actually, the sizes and shapes of Ag NPs are random. Therefore, the SERS

active surface area was about 1.3 times the value of a simple Ag flat layer. The value of N_{SERS} is the product of the packing density × the surface area ratio (1.3), yielding 1.6×10^7 molecules. N_{Raman} was calculated using the confocal volume (18.9 μm^3), BT density (1.08 g/mL), and molecular weight (110.19 g/mol), yielding a value of 1.1×10^{11} molecules. Therefore, N_{Raman}/N_{SERS} was 6.9×10^3.

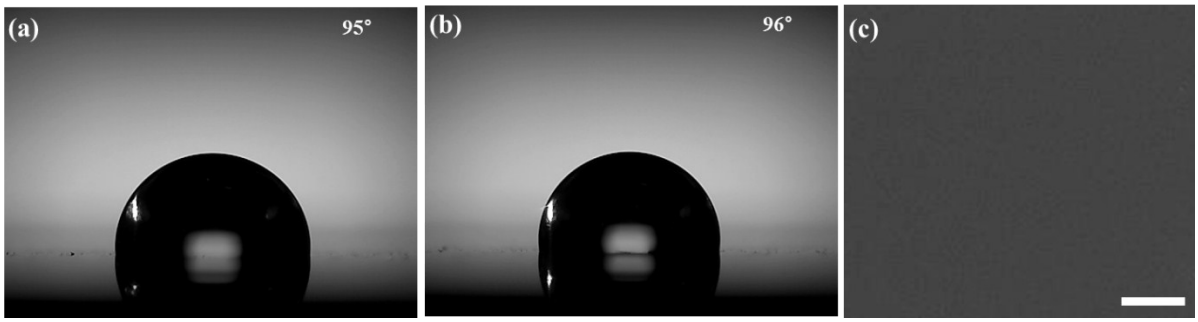

Fig. S2 Change of water contact angles on the smooth alumina thin films (a) before and (b) after PFDT treatments. The contact angles remained unchanged upon PFDT vapor treatment. (c) surface morphologies of 50 nm thick alumina thin films. The scale bar is 1 μm.

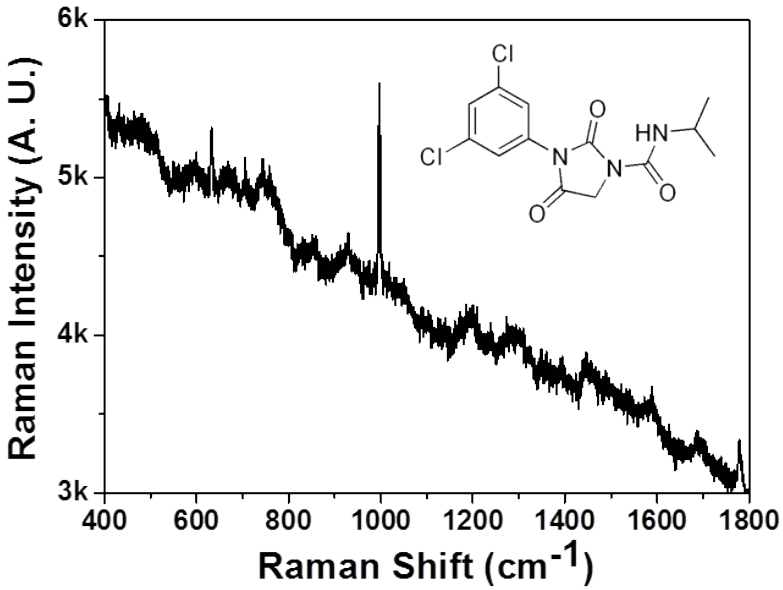

Fig. S3 Raman spectrum of iprodione powder. Inset shows the chemical structure of iprodione molecule. . Iprodione is characterized by a major peak at 1000 cm^{-1}, which corresponds to a benzene breathing mode.

1 T. Y. Jeon, S.-G. Park, D.-H. Kim and S.-H. Kim, *Adv. Funct. Mater.*, 2015, **25**, 4681–4688.

2 S.-G. Park, C. Mun, M. Lee, T. Y. Jeon, H.-S. Shim, Y.-J. Lee, J.-D. Kwon, C. S. Kim and D.-H. Kim, *Adv. Mater.*, 2015, **27**, 4290–4295.

Video 1. Placing a 8-µl water droplet on the 3D superhydrophobic SERS surface. This video show that placing a 8-µl water droplet on the 3D superhydrophobic SERS surface is very difficult due to the slippery nature of the surface.

Video 2. Penetration of water drop into as-prepared 3D porous Ag nanostructures. The water drop soaked into the as-prepared 3D SERS substrates. The water soaked into both the stacked Ag NWs (thickness ≈0.20 µm) and a glass microfiber filter (thickness ≈ 420 µm) within 2 sec.

Video 3. Complete wetting of acetone into as-prepared 3D porous Ag nanostructures. The 3D porous Ag nanostructures show a complete wetting of acetone with CA of 0°.