Superhydrophobic SERS Substrates based on Plasmonic Hierarchical Micro-nanostructures

Junyeob Song[1], Weifeng Cheng[2], Jiangtao Cheng[2],* and Wei Zhou[1, *]
[1]*Bradley Department of Electrical & Computer Engineering, Virginia Tech, Blacksburg, Virginia 24061, USA*
[2]*Department of Mechanical Engineering, Virginia Tech, Blacksburg, Virginia 24061, USA*
**Email: chengjt@vt.edu; wzh@vt.edu*

Abstract: Integration of multilayered plasmonic nanostructures with hierarchical micro-nanopillar arrays can result in a superhydrophobic surface with high-performance Surface Enhanced Raman Spectroscopy (SERS) functionality.

OCIS codes: (250.5403) Plasmonics; (240.6695) Surface-enhanced Raman scattering; (350.4238) Nanophotonics and photonic crystals

1. Summary

Nanoplasmonic systems have been studied to concentrate light within sub-nm scale adjacent to metal-dielectric interfaces [1]. Due to orders-of-magnitude higher local field enhancement, plasmonic nanostructures can achieve Surface Enhanced Raman Spectroscopy (SERS) for chemical and biological sensing purposes [2-4]. In particular, SERS devices can detect and identify analytes at single molecule level if the SERS enhancement factor (EF) is higher than 10^7 [5]. Recently, we developed a new type of nanoplasmonic quasi-3D crystals based upon multilayered metal-insulator-metal nanostructures, which supports multiple plasmon modes induced by hybridization between Bloch surface plasmon polaritons and localized gap plasmon modes [6]. Such multiresonant plasmonic systems can enable simultaneous enhancement of excitation and emission processes for SERS applications [7].

Digital microfluidic (DMF) systems based on electrowetting have been developed to provide lab-on-a-chip applications [8]. By applying electric signals, the analyte droplets can be adaptively manipulated and transported in DMF systems. Compared to conventional continuous microfluidics through microchannels, DMF can offer unique advantages, such as the compact and scalable design without the use of pumps/valves/mixers, the highly reconfigurable and programmable nature using arrays of electronic components, the clogging-free architecture by eliminating microchannels, and lower power consumption. Previous study has shown that two-tier hierarchical micro-nanostructures can result in superhydrophobic surfaces for improved manipulation of droplets in a electrowetting-based DMF system [9].

Here we demonstrated a superhydrophobic SERS substrates composed of multilayered Au-Ag-Au nanostructures on hierarchical micro-nano pillar arrays, which provides both conductive superhydrophobic surface and good SERS enhancement to enable bio-chemical SERS analysis in DMF systems (Fig 1A-B). The passive optical properties of multilayered Au-Ag-Au metal nanostructures on hierarchical micro-nanostructures made of carbon nanopillars and hydrophobic Si micropillars show broadband absorption properties in visible to NIR region compared to other references as shown in Fig. 1C. We measured the contact angle of water droplet on the sample of hierarchical micro-nanostructures with multilayered Au-Ag-Au coating and the droplet profile showed high contact angle (140°), which is associated with the low surface energy of the hydrophobic side walls for the hierarchical structures made of carbon nanopillars and hydrophobic Si micropillars. We performed Raman spectroscopy characterization using benzenethiol (BZT) for all samples and we found that Au-Ag-Au nanostructures on hierarchical micro-nanopillar arrays only show strong BZT Raman features showing SERS enhancement factor of 10^7 (Fig. 2B and 2D). The uniformity was also studied by checking the 2D confocal Raman spectroscopy mapping and it confirmed the contribution of the SERS enhancement is from the entire area. The statistical analysis of 2D SERS mapping at five different positions on the sample also supports a good uniformity of SERS performance for the samples (Fig. 2D). Therefore, such superhydrophobic SERS substrates by integrating nanoplasmonic devices with hierarchical micro-nanopillar structures with low surface-energy side walls can serve as a key component in functional DMF systems for programmable and reconfigurable bio-/chemical sensing applications.

2. Figures

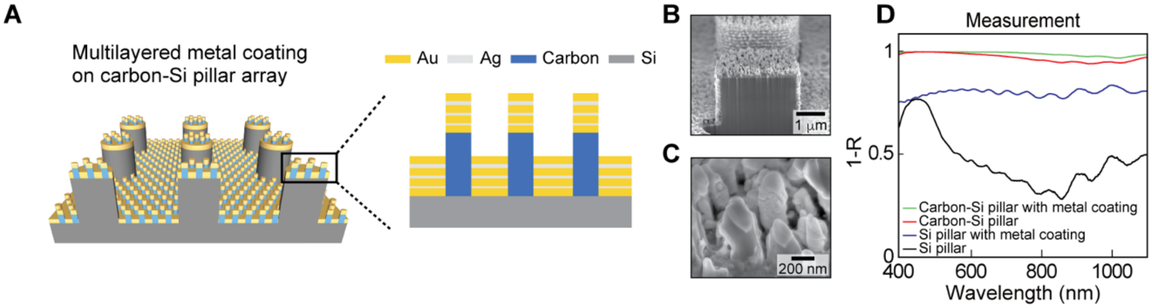

Figure 1. (A) Schematic illustration of multilayered Au-Ag-Au metal nanostructures on hierarchical micro-nanostructures made of carbon nanopillars and hydrophobic Si micropillars. (B-C) SEM cross-section images of hierarchical micro-nanostructures deposited with multilayered Au-Ag-Au metal layers. (D) Measured reflectance spectra of hierarchical micro-nanostructures deposited with multilayered Au-Ag-Au layers (green curve) and reference samples: hierarchical micro-nanostructures without multilayered Au-Ag-Au coating (red curve), Si micropillar arrays with multilayered Au-Ag-Au coating (blue curve), and bare Si pillar arrays (black curve).

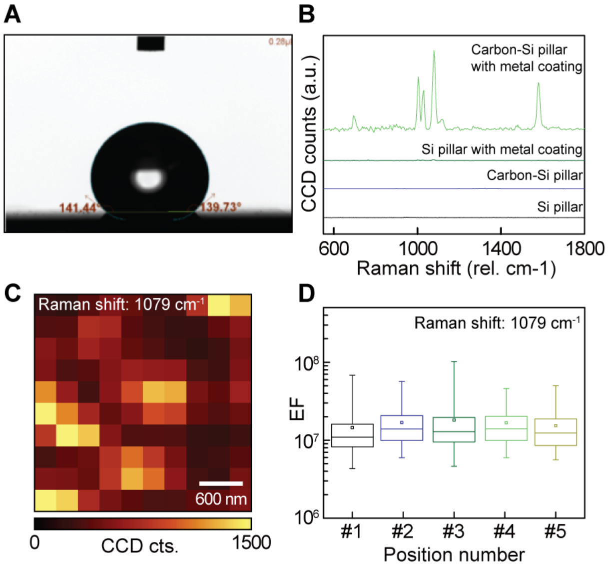

Figure 2. (A) Contact angle measurement of water droplet on hierarchical micro-nanostructures deposited with multilayered Au-Ag-Au metal layers. (B) Raman spectra of benzenethiol (BZT) from hierarchical micro-nanostructures deposited with multilayered Au-Ag-Au metal layers in comparison with those from reference samples. (C) Confocal Raman images for BZT signals at 1079 cm^{-1} from hierarchical micro-nanostructures deposited with multilayered Au-Ag-Au metal layers. (D) The SERS enhancement factors (EFs) for the sample of hierarchical micro-nanostructures deposited with multilayered Au-Ag-Au metal layers measured at five different positions. Raman intensity at 1079cm^{-1} was used to calculate. Lines in error bars show values of minimum, 25%, median, 75%, and maximum, and a small box shows the mean value.

3. References

[1] W. L. Barnes, A. Dereux, and T. W. Ebbesen, "Surface plasmon subwavelength optics," Nature **424**, 824 (2003).

[2] S. S. R. Dasary, A. K. Singh, D. Senapati, H. Yu, and P. C. Ray, "Gold Nanoparticle Based Label-Free SERS Probe for Ultrasensitive and Selective Detection of Trinitrotoluene," J. Am. Chem. Soc. **131**, 13806-13812 (2009).

[3] D. A. Stuart, J. M. Yuen, N. Shah, O. Lyandres, C. R. Yonzon, M. R. Glucksberg, J. T. Walsh, and R. P. Van Duyne, "In Vivo Glucose Measurement by Surface-Enhanced Raman Spectroscopy," Anal. Chem. **78**, 7211-7215 (2006).

[4] J.-F. Li, Y. F. Huang, Y. Ding, Z. L. Yang, S. B. Li, X. S. Zhou, F. R. Fan, W. Zhang, Z. Y.3 Zhou, D. Y. Wu, B. Ren, Z. L. Wang, and Z.-Q. Tian, "Shell-isolated nanoparticle-enhanced Raman spectroscopy," Nature **464**, 392-395 (2010).

[5] A. Otto, "On the significance of Shalaev's 'hot spots' in ensemble and single-molecule SERS by adsorbates on metallic films at the percolation threshold," J. Raman Spectrosc. **37**, 937-947 (2006).

[6] J. Song, W. Nam, and W. Zhou, "Multiresonant Optical Response in Quasi-3D Multilayer Metal-Insulator-Metal Plasmonic Nanostructures," in Conference on Lasers and Electro-Optics, OSA Technical Digest (online) (Optical Society of America, 2018), paper STh1A.3.

[7] T. Itoh, K. Yoshida, V. Biju, Y. Kikkawa, M. Ishikawa, and Y. Ozaki, "Second enhancement in surface-enhanced resonance Raman scattering revealed by an analysis of anti-Stokes and Stokes Raman spectra," Phys. Rev. B **76(8)**, 085405 (2007).

[8] M. G. Pollack, A. D. Shenderov, and R. B. Fair, "Electrowetting-based actuation of droplets for integrated microfluidics," Lab Chip **2**, 96-96 (2002).

[9] J. Cheng, A. Vandadi, and C.-L. Chen, "Condensation heat transfer on two-tier superhydrophobic surfaces," Appl. Phys. Lett. **101**, 131909 (2012).