

Supporting Information for “Superhydrophobic Surface Enhanced Raman Scattering Sensing using Janus Particle Arrays Realized by Site-Specific Electrochemical Growth”

Shikuan Yang,^{*,a} Patrick John Hricko,^a Po-Hsun Huang,^a Sixing Li,^a Yanhui Zhao,^a Yuliang

Xie,^a Feng Guo,^a Lin Wang,^b and Tony Jun Huang^{*,a}

^aDepartment of Engineering Science and Mechanics, The Pennsylvania State University,

University Park, PA 16802, USA

E-mail: szy2@psu.edu; junhuang@psu.edu

^bAscent Bio-Nano Technologies Inc., State College, PA, 16801, USA

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Part I. Experimental Section

A. Fabrication of MCC templates

MCC templates composed of different sized polystyrene (PS) spheres were prepared by a spin-coating method. Briefly, glass slides (1 cm x 1 cm) were cleaned in turn with acetone, ethanol, deionized water, 98% $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ (3:1), $\text{H}_2\text{O}/\text{NH}_3 \cdot \text{H}_2\text{O}/\text{H}_2\text{O}_2$ (5:1:1), and distilled water in order to obtain superhydrophilic surfaces. 10 μL of the suspension of monodisperse PS spheres (purchased from Alfa Aesar, negatively charged, 2.5 wt % in water) with different sizes was pipetted onto the cleaned glass slide. After 10 min of spin-coating under the speed of 400 (for 2 μm sized PS spheres) and 600 (for 1 μm sized PS spheres) round/min, highly uniform MCC templates were prepared. Subsequently, the glass slide covered by the MCC template was immersed very slowly into deionized water. The MCC template was peeled off from the glass slide and floated on the water surface (Scheme S1A). The MCC template underwent a further assembly process, during which most of the defects formed during the spin-coating process were remediated. Another arbitrary substrate could be used to pick up the floating MCC template (Scheme S1B, C). Thermal evaporation of gold film on the MCC templates was conducted with a Kurt Lesker Lab-18 evaporator at a rate of 0.1 nm/s. The as-prepared MCC template covered by the thin layer of Au film was used as the electrode to conduct the ECD growth of different materials.

B. Site-specific ED parameters

Electrochemical deposition (ED) was carried out under potentiostatic mode within a two-electrode cell. A piece of Si wafer (area: 1 cm x 2 cm) was used as the anode electrode. Electrochemical deposition of Ag was conducted in the electrolyte solution containing 2 g/L sodium dodecyl sulphite and 10 g/L AgNO₃. The deposition voltage for Ag was 6 V. The deposition time of Ag varied from 1 min to 30 min, in order to study the site-specific ED growth process. 0.4 g CuSO₄·5H₂O was added to 40 ml deionized water together with 0.4 g H₃BO₃ for Cu (a little amount of CuOx, 0 < x < 2, was involved) deposition under the voltage of 2 V. The Cu deposition process lasted for 2 min. A 50 nm-thick Au layer covered MCC template was used to prepare the multi-component PS-Au/Pt/ZnO Janus particle arrays depending on the step-by-step electrochemical deposition concept. The Pt layer deposition was conducted for 2 min under the voltage of 5 V in the electrolyte made by dissolving 2.5 g H₂PtCl₆ into 1 L deionized water. Subsequently, ZnO was further deposited under the voltage of 5 V for 10 min in 0.01 M Zn(Ac)₂ aqueous solution.

C. SERS measurements

10 µL aqueous solutions of R6G (Rhodamine 6G), protein, and virus with different concentrations were dropped on the superhydrophobic PS-Ag Janus particle array before SERS detections in order to evaluate the SSERS performance. A 488 nm laser was used for the SERS measurements. The laser power was about 0.2 mW. The accumulation time was 10 s.

D. Origin of the Raman peaks of protein and virus

Origin of the Raman peaks from PV RdRp protein and PV type I Sabin virus is shown in Table

S1 and S2, respectively.

SSERS	Band Assignment	References
635	guanine	S1
725	adenine	S1
843	Tyr	S1,S2
923	Stretching mode of C-C	S3
1010	Phe	S1
1055	Phe	S2
1214	Tyr	S2
1461	CH ₂ deformation	S1,S5

Table S1. Band assignment of PV RdRp.

SSERS	Band Assignment	References
650	guanine	S1
833	Tyr; O-P-O symmetric stretch	S3
863	Tyr	S1
1046	Phe; ribose; Phenylalanine	S3
1140	Stretching vibration of C-C	S1
1293	Amide III from protein	S4
1464	Amide II; CH ₂ deformation; C-N stretching mode	S5

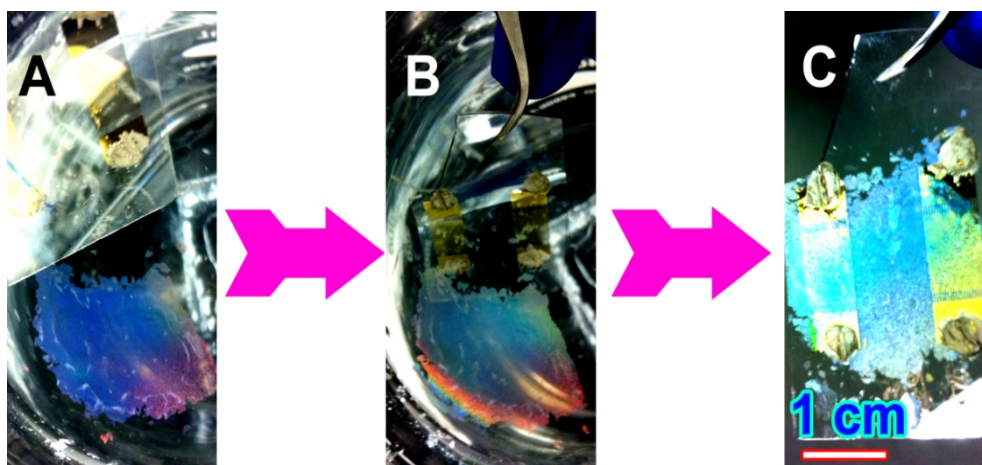
Table S2. Band assignment of PV type I Sabin.

References:

- S1: S. Shanmukh, L. Jones, J. Driskell, Y. Zhao, R. Dluhy, R. A. Tripp, *Nano Lett.* **2006**, 6, 2630.
S2: C. Blum, T. Schmid, L. Opilik, N. Metanis, S. Weidmann, R. Zenobi, *J. Phys. Chem. C* **2012**, 116, 23061.
S3: T. A. Turano, K. A. Hartman, *J. Phys. Chem.* **1976**, 80, 1157.
S4: W. T. Cheng, M. T. Liu, H. N. Liu, S. Y. Lin, *Microsc. Res. Tech.* **2005**, 68, 75.
S5: Z. Movasaghi, S. Rehman, I. U. Rehman, *Appl. Spectrosc. Rev.* **2007**, 42, 493.

Part II. Supporting Figures

Fabrication process of the MCC template is schematically shown in Scheme S1. After thermal evaporation of Au film on the MCC template, only the top surfaces of the PS spheres were covered by the Au layer due to the shadow effects, as shown in Figure S1.



Scheme S1. Fabrication process of the MCC template. (A) MCC template floating on the water surface. (B) After picking up the MCC template by a substrate. (C) Highly ordered MCC template with an area of up to 2 cm x 2 cm.

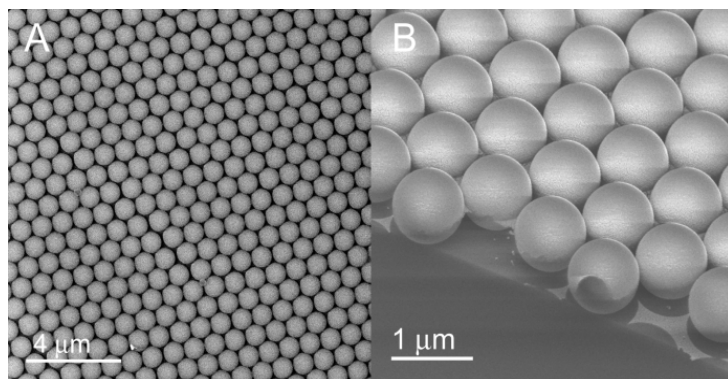


Figure S1. (A) SEM image of the MCC template. (B) SEM image of the MCC template after thermal evaporation of the Au layer.

Using an MCC template without the gold layer as an electrode to conduct ED of Ag, macroporous Ag film was obtained.

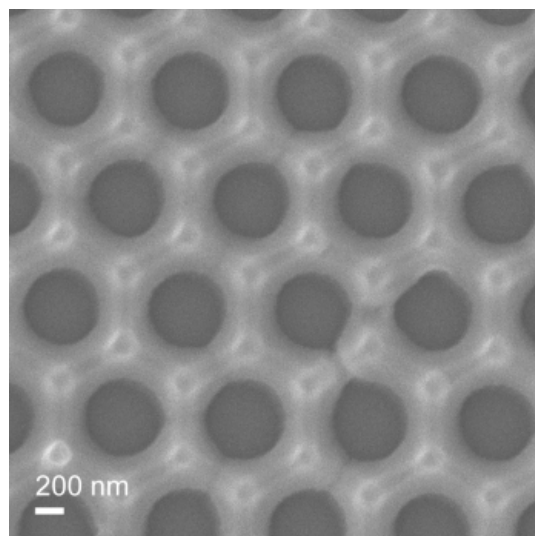


Figure S2. Macroporous Ag film obtained by ED using an MCC template.

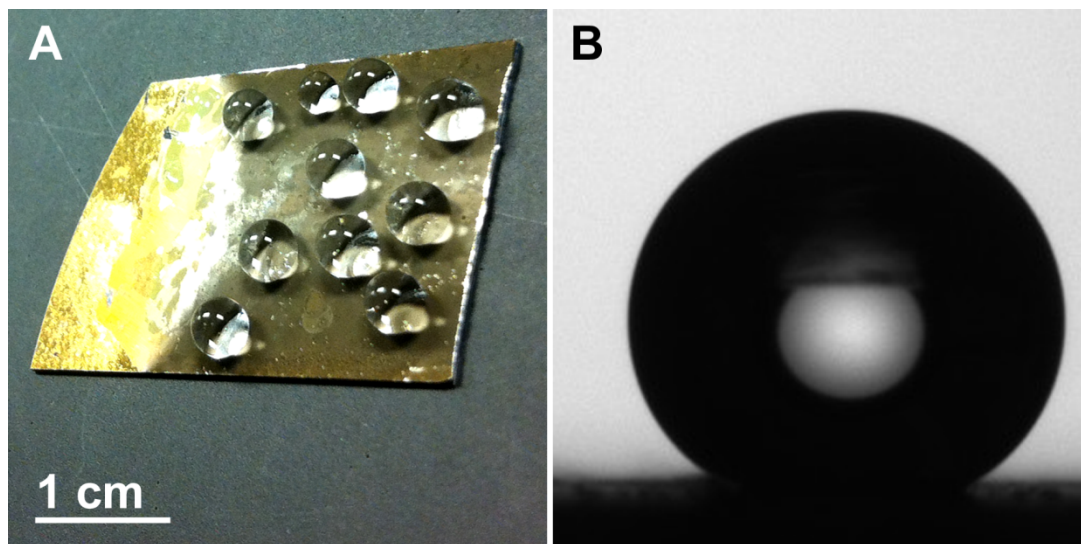


Figure S3. (A) Photography of ten water droplets on the SSERS substrate. (B) Contact angle measurement.

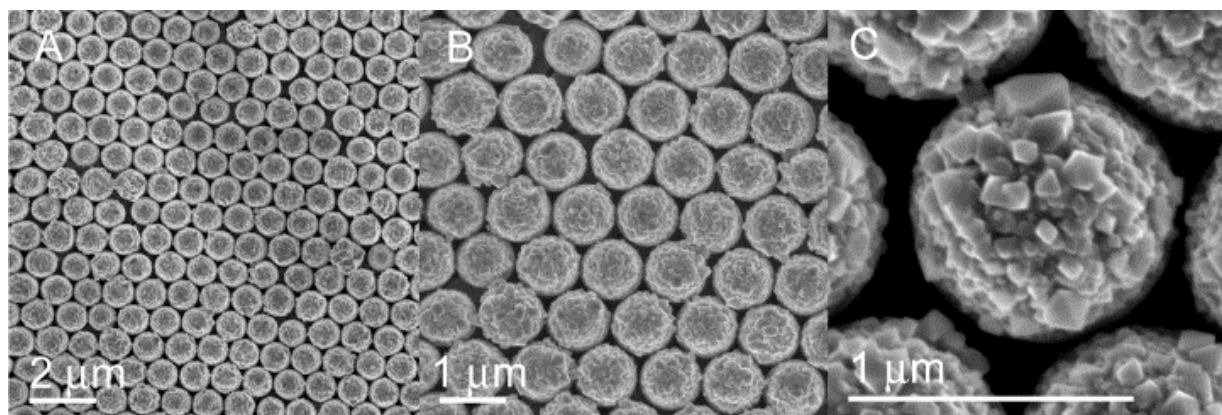


Figure S4. Site-specific ED growth to PS-Cu Janus particles with one side formed by many Cu octahedrons, which cannot be realized by the other techniques.

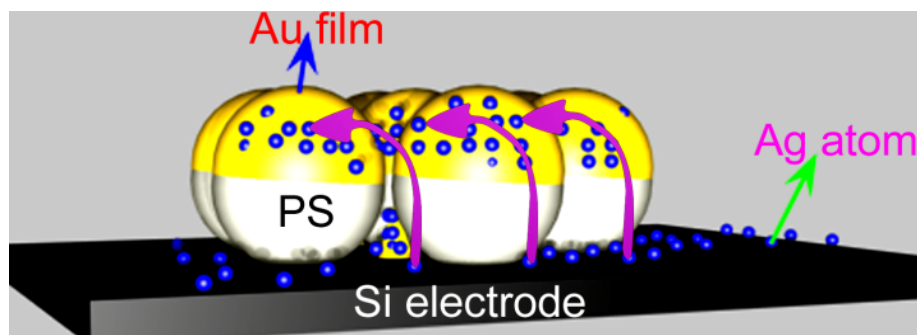


Figure S5. Schematic demonstration of the atom migration process and site-specific growth during ED process