Supporting Information for

Electrochemically synthesized porous Ag double-layers for SERS applications

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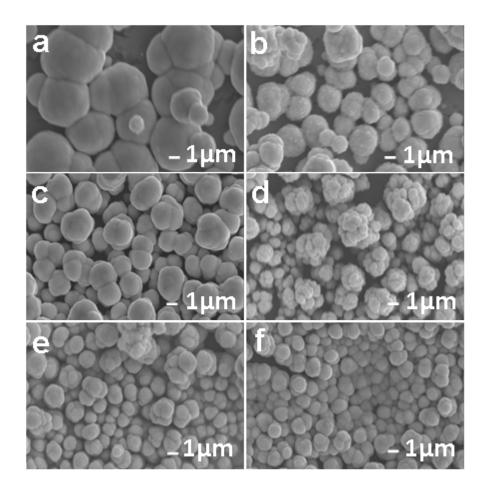


Figure S1. SEM images of AgCu alloy electrodeposited at a) - 0.2 V; b) -0.3 V; c) -0.4 V; d) -0.5 V; e) -0.6 V; (f) -0.7 V. The scale bar: 1 μ m.

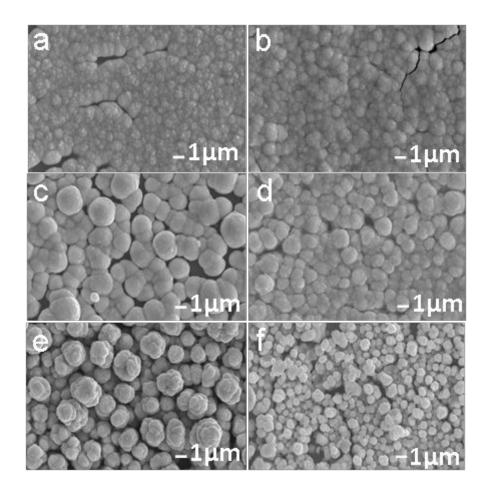


Figure S2. a) SEM images of AgCu alloy electrodeposited with saccharin ($C_7H_5NO_3S$) added in the electrolyte at a) -0.2 V; b) -0.3 V; c) -0.4 V; d) -0.5 V; e) -0.6 V; f) -0.7 V. The scale bar: 1 μ m.

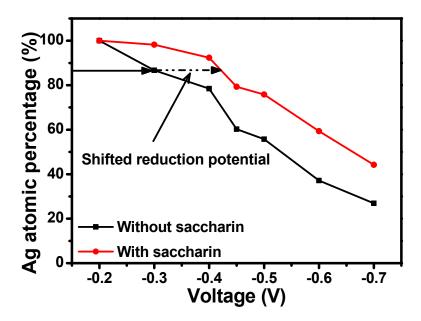


Figure S3. Silver content of the AgCu alloy electrodeposited with or without saccharin added in the electrolyte.

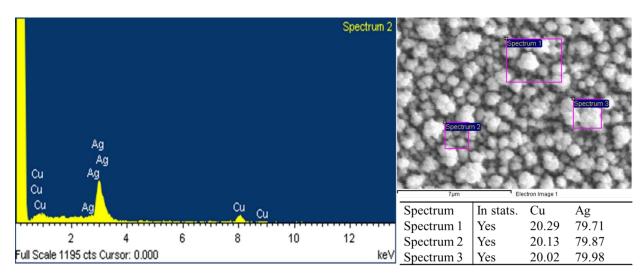


Figure S4. EDX spectrum and the corresponding SEM image of the AgCu alloy electrodeposited at -0.4 V.

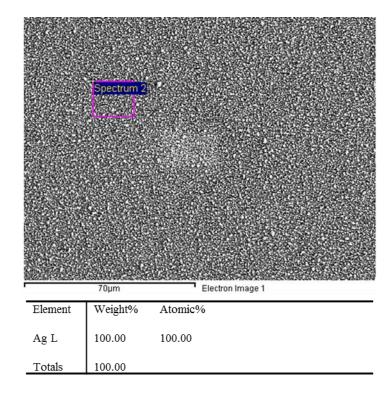


Figure S5. The EDX measurement result and the corresponding SEM image of the AgCu alloy after dealloyed in diluted H_2SO_4 (0.05 M).

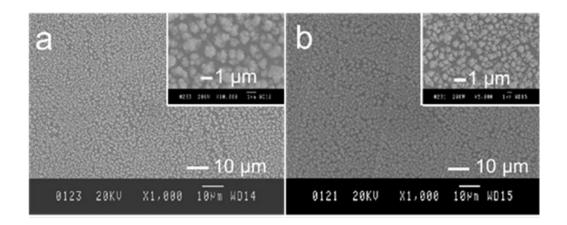


Figure S6. Top-view SEM images of the electrodeposited double layers with higher Cu content in the top (a) or bottom (b) layer (before dealloy treatment).

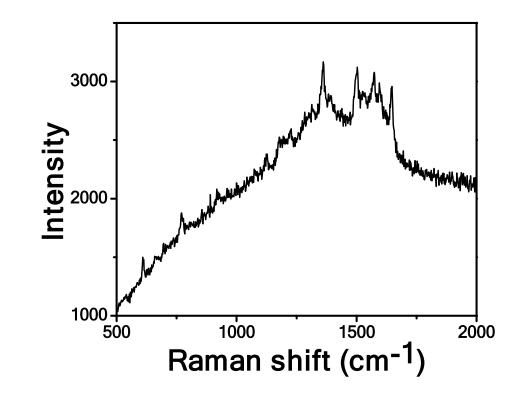


Figure S7. The Raman spectrum of Rhodamine 6G (10-2 M) on silicon wafer.

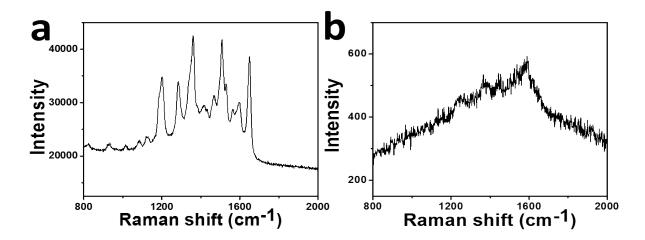


Figure S8. The Raman spectra taken on the double layered film with big pores at top that was pre-soaked in the Rhodamine b (10⁻⁶ M) solution, before (a) and after (b) sonication in water.

Calculation of enhancement factor (EF)

The enhancement factor (*EF*) is calculated from the experimental results. The *EF* values of porous Ag films were determined using Rhodamine 6G (R6G) as probe:

$$EF = (I_{SERS} / N_{SERS}) / (I_{bulk} / N_{bulk})$$

Where N_{SERS} and N_{bulk} are the number of R6G molecules probed on the porous Ag film and on silicon wafer, respectively; I_{SERS} and I_{bulk} are the Raman peak intensity of R6G at 1650 cm⁻¹. N_{bulk} was calculated based on the concentration of the R6G aqueous solution (10⁻² M) and the Raman scattering volume (the laser spot is ca. 2 μ m in diameter and the penetration depth is ca. 20 μ m) (Fig. S8). Similarly, N_{SERS} is calculated from the concentration of the R6G aqueous solution (10⁻⁸ M) and the drop volume (2 μ l) on the sample.