Supplementary Information

Well-Organized Raspberry-like Ag@Cu Bimetal Nanoparticles for Highly Reliable and Reproducible Surface Enhanced Raman Scattering

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Experimental:

Materials: Silver nitrate ($AgNO_3$) and copper nitrate ($Cu(NO_3)_2$) were obtained from Alfa Aesar and Sigma-Aldrich, respectively. Polyvinyl pyrrolidone (PVP, Mw = ~55,000 g/mol) and ethylene glycol (EG, anhydrous, 99.8%) were purchased from Sigma-Aldrich for the synthesis of silver nanoparticles. Hydrazine (anhydrous, 98%) from Sigma-Aldrich was used as a reducing agent. R6G was supported from TCI-Ace. All of the chemicals were used without further treatment.

Preparation of raspberry-like Ag@Cu nanostructures: The raspberry-like Ag@Cu bimetals were obtained by a stepwise reducing method. In a typical procedure, 0.75 g of PVP was dissolved in 3 mL of EG, and then $AgNO_3$ (0.25 g) was added into the resulting solution at room temperature. The mixture was heated up to 120 °C and kept for 1 hr under vigorous stirring. After complete reduction of $AgNO_3$ to Ag nanoparticles, 15 mL of ethanol was added into the as-prepared Ag solution. $Cu(NO_3)_2$ solution in ethanol (0.5 g/mL) was stirred with the homogeneous Ag colloidal dispersion. The raspberry-like Ag@Cu bimetal nanoparticles were formed by reducing with hydrazine at room temperature. For the preparation of Ag@Cu core@shell nanostructures, formaldehyde solution (0.5 mL) was added into a colloidal solution of the as-synthesized raspberry-like Ag@Cu nanostructures, subsequently followed by addition of ammonium hydroxide (28% 0.5 mL). The colloidal solutions of the bimetal nanostructures were then centrifuged at 6000 rpm for 20 min with excess deionized water and ethanol to remove other additives.

Characterizations: As-prepared Ag@Cu raspberries coated on a clean Si wafer were characterized using a scanning electron microscope (SEM, Leo/Zeiss 1530). The Ag@Cu samples dispersed in ethanol by ultrasonication for 30 min were transferred onto Formvar-coated copper grids for microanalysis using a transmission electron microscope (TEM, JEM-1400) operated at an accelerating voltage of 120 kV. Absorption spectra of Ag@Cu samples

(coated on a clean cover glass) were collected using a UV-Vis-NIR spectrometer (Ocean Optics) with a wavelength ranging from 200 to 1200 nm. To prepare the samples for Raman characterization, we mixed the solution containing the SERS nanoparticles with the R6G (10^{-3} M) solution in ethanol (1:1 volume ratio). Then, 10 μL Ag@Cu and R6G mixed solution was spin coated on a silicon wafer (1x1 cm^2). The concentration of the R6G molecules should be ~$5x10^{-9}$ M/cm^2. Raman spectra were acquired using a Renishaw RM 1000 spectroscopy system (~2 μm spot size). Argon lasers emit at the wavelengths of 488 nm and 514 nm (Melles Griot). Also, a solid state laser emitting at 633 nm (Thorlabs HRP170) were used for excitation with the laser power set below 3 mW to prevent potential overheating. All Raman spectra presented here were averaged from 7–9 points collected by a mapping function provided by Renishaw system, so as to improve the data reliability. An automated MATLAB program was developed to remove the fluorescence background present in the Raman spectra with a protocol developed by Lieber et al.[30]

Supplementary Figures and Discussion

1. Morphology of Ag nanoparticles:

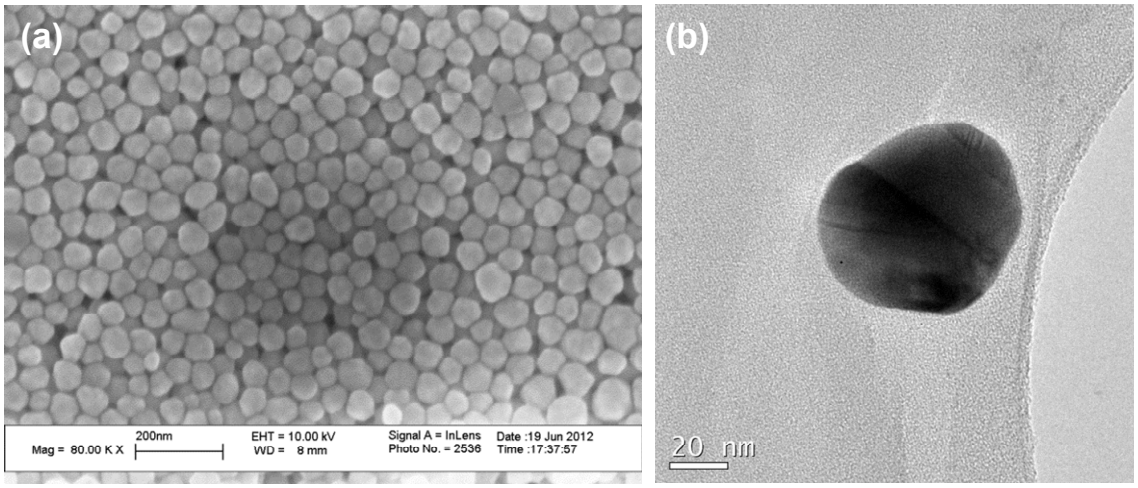

Fig. S1. Typical morphologies of the Ag nanoparticles prepared by a polyol method: (a) SEM and (b) TEM image.

2. Typical morphologies of Ag@Cu core@shell nanoparticles

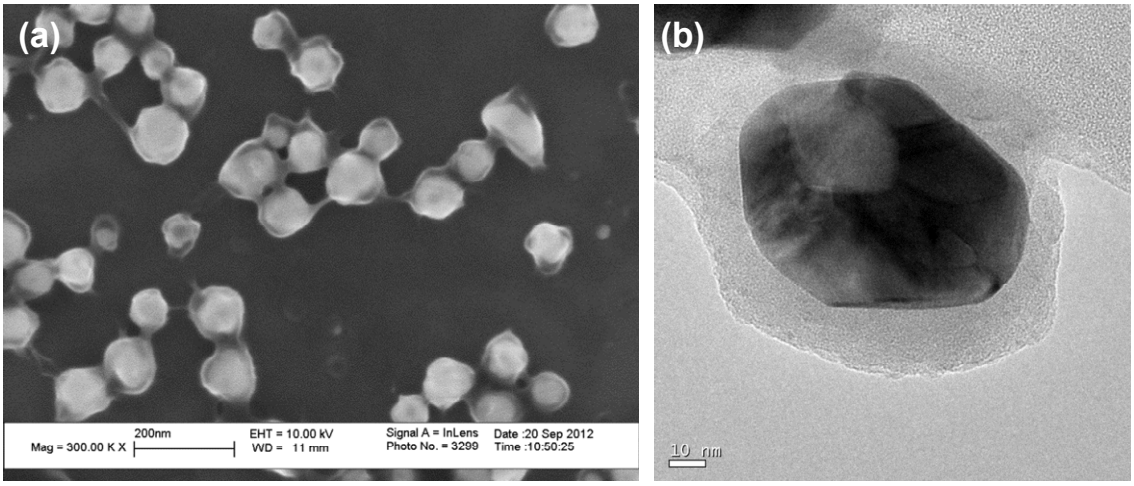

Fig. S2. Typical morphologies of the Ag@Cu core@shell nanoparticles: (a) SEM and (b) TEM image.

3. HR-TEM image and XRD patterns of the raspberry-like Ag@Cu bimetal nanostructures:

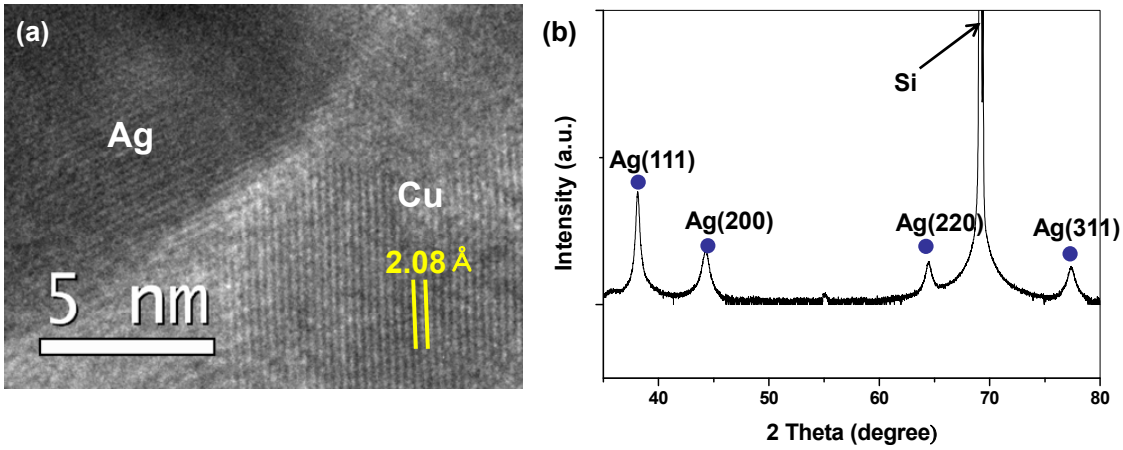

Fig. S3. (a) HR-TEM image and (b) XRD patterns of the raspberry-like Ag@Cu bimetal nanostructures coated on a clean silicon substrate.

4. UV-Vis absorption spectra of the raspberry-like Ag@Cu bimetal nanoparticles

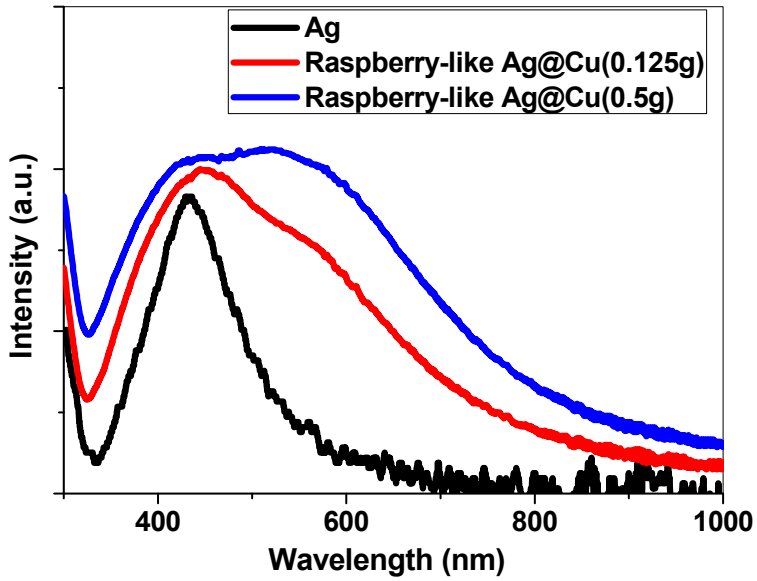

Fig. S4. Comparison of UV-Vis absorption spectra of the Ag nanoparticles and the raspberry-like Ag@Cu bimetal nanoparticles with different Cu to Ag ratios.

5. The calculation of enhancement factor (EF)

The enhancement factor is calculated using the method proposed by Li et al.[14]

$$EF = \frac{I_{SERS}/N_{SERS}}{I_{Normal}/N_{Normal}}$$

The intensity (I) was obtained by integration of the main peak of R6G from 1620 to1680cm^{-1}.

N is the number of the R6G molecules, which was estimated from the surface concentration.

6. Reproducibility of SERS spectra of R6G with the SERS-active particles

All Raman spectra presented here were the average of the data collected from 7–9 points using a mapping function provided by Renishaw system to improve the data reliability.

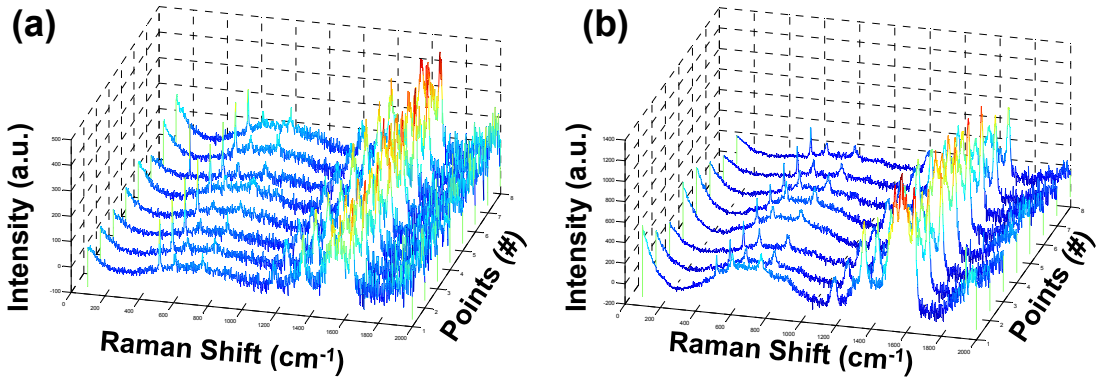

Fig. S5. SERS spectra of R6G with the SERS-active particles of (a) core@shell and (b) raspberry nanoparticles collected at several points**.**

7. Stability of SERS spectra of R6G with the Ag@Cu nanoraspberries

In order to test the stability of surface enhancing effect of Ag@Cu raspberry nanoparticles, we test the Raman spectra of R6G (10^{-3}M) with spin-coated Ag@Cu raspberry nanoparticles after 60 days of exposure to the air under the same configuration of laser power. It is found that the spectra of the sample after 60 days of exposure have little difference with the spectra of as-synthesized sample, proving the reliability of the Ag@Cu raspberry nanoparticles.

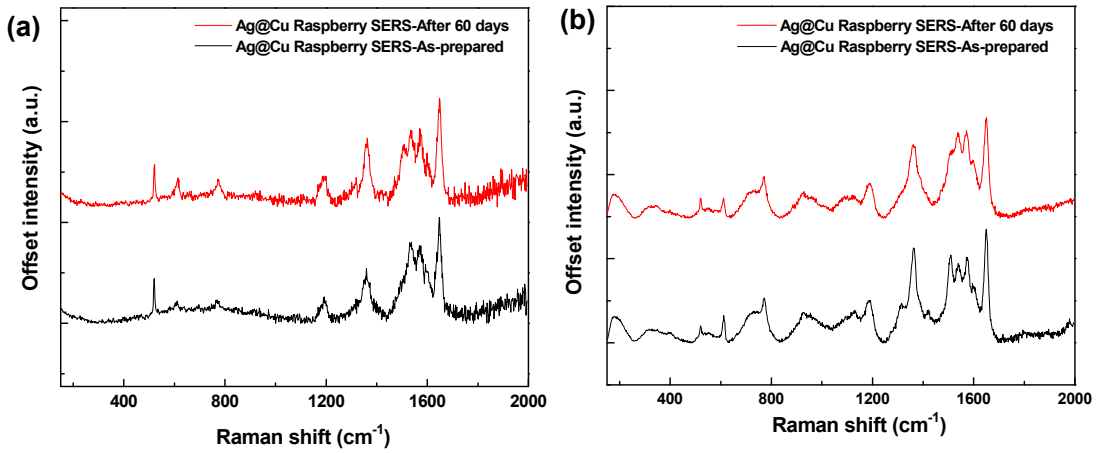

Fig. S6. SERS spectra of R6G with the Ag@Cu raspberry nanoparticles collected under (a) 488 nm and (b) 514 nm excitation source after 60 days from as-prepared**.**

8. SERS spectra of R6G with the SERS particles prepared by different coating method

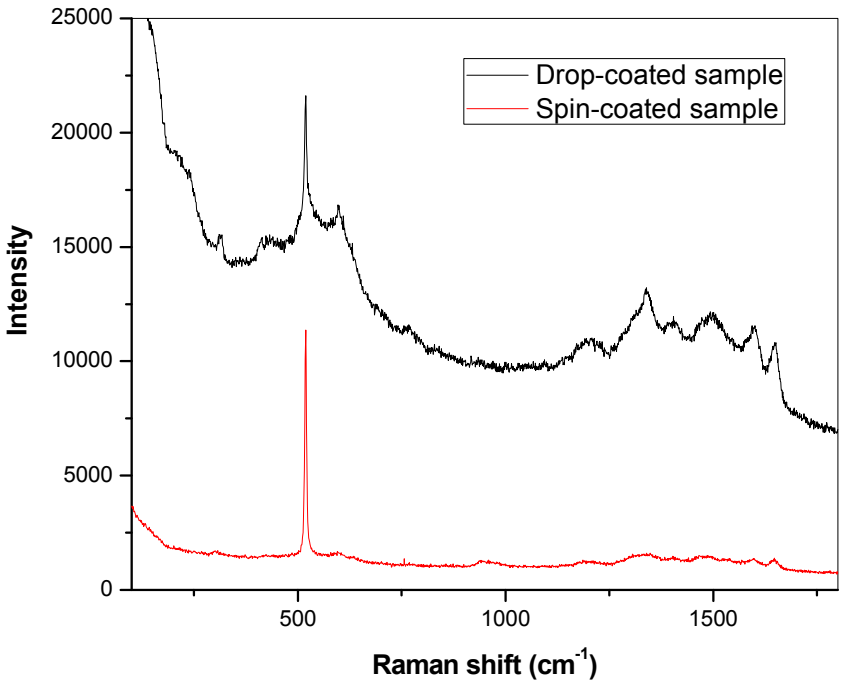

Fig. S7. SERS spectra of R6G with the raspberry-like Ag@Cu bimetal nanoparticles prepared using a spin-coating and a drop-coating method.

9. GDC thin film on a silicon substrate

Gd-doped ceria (GDC) thin films were deposited on silicon wafers through RF magneton sputtering. The GDC target was home made by dry pressing and sintering of commercial GDC powders (Topsoe) at 1450 °C for 5 hours. As calibrated by cross-section SEM images, the standard 3 hour deposition protocol resulted in a thickness of about 80 nm. The subsequent annealing at 800 °C for 30 min increased the crystallinity of the GDC films.

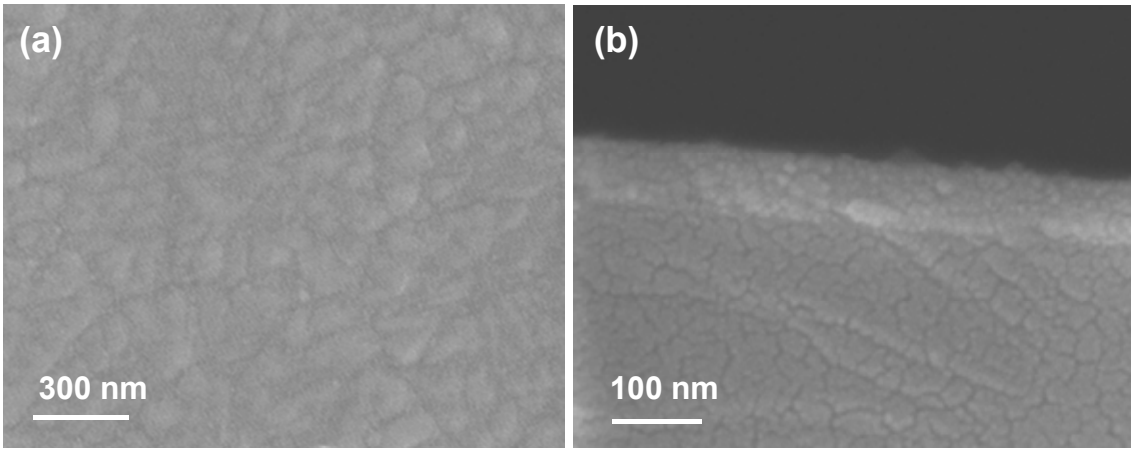

Fig. S8. SEM images of the GDC films deposited on a silicon wafer: (a) surface and (b) cross-sectional view.