

Supporting Information

Superhydrophobic SERS chip based on Ag coated natural taro-leaf

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Chlorophyll photobleaching by sunlight irradiation

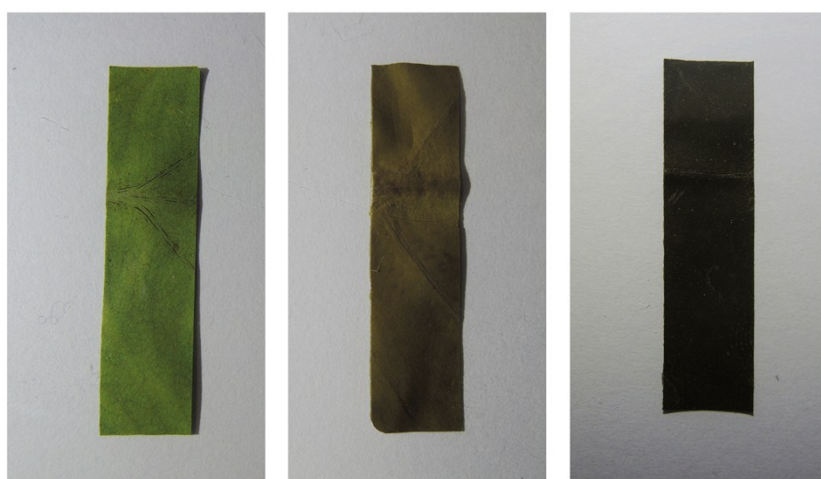
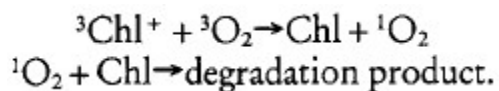


Figure S1 Sunlight irradiation turn the fresh green taro leaf (left) to yellow (middle) and brown (right); the color change indicates the decomposition of chlorophyll in the leaf which suppresses the chlorophyll fluorescence.

The light-induced chlorophyll (Chl) degradation reaction by photosynthesis-produced singlet oxygen on leaves is generally accepted as:¹



This chlorophyll photobleaching will occur when energy transfer from excited triplet chlorophyll to carotenoid molecules in thylakoid membranes is suppressed.

The energy transfer efficiency depends significantly upon the distance and the

mutual orientation between chlorophyll and carotenoid molecules. The heat of strong sunlight will lead to temperature rise on thylakoid membranes that will enlarge the distance and orientation between the chlorophyll and the carotenoid molecules as well as lead to structure change of the thylakoid membrane, thus resulting to low energy transfer efficiency.¹ Therefore, the chlorophyll photobleaching is enhanced when the taro leaf is irradiated by the strong sunlight that generates much heat.

The silver deposition on the Taro leaf

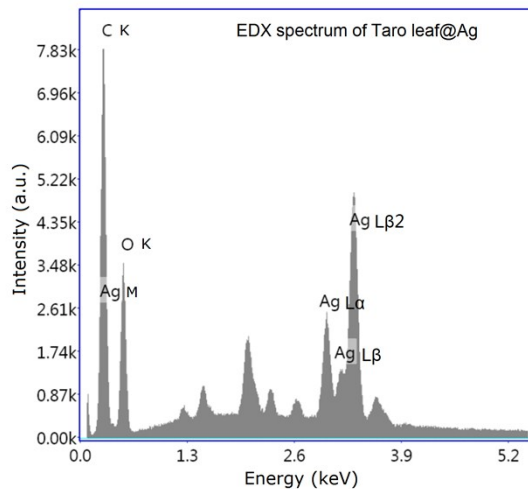


Figure S2. EDX spectrum of Taro leaf@Ag.

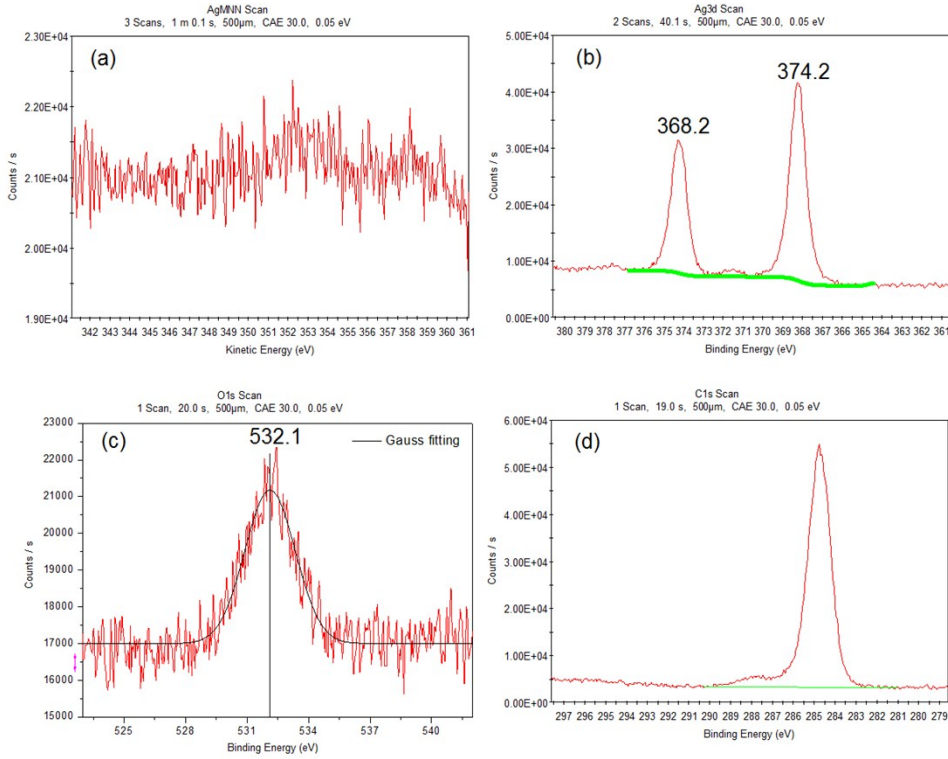


Figure S3. XPS spectra of Taro leaf@Ag. (a) AgMNN scan; (b) Ag3d scan indicates the binding energy of Ag 3d_{3/2} and Ag 3d_{5/2} at 368.2 eV and 374.2 eV, respectively. The 6 eV splitting between them indicates the Ag is at Ag⁰ state, which implies that the Ag has experienced negligible oxidization.²; (c) O 1s scan indicates C-OH peak at 532.1 eV; (d) C 1s scan.

Enhancement Factor calculation

Assuming the R6G molecules uniformly distribute on the contact area when a droplet of R6G solution is dried on the Taro leaf@Ag, we use following formula to calculate the enhancement factor (EF):

$$EF = \frac{I_{SERS} / N_{SERS}}{I_{RS} / N_{RS}} = \frac{I_{SERS} \times N_{RS}}{I_{RS} \times N_{SERS}} = \frac{I_{SERS}}{I_{RS}} \frac{D \times H_{eff} \times \rho_v}{D \times \rho_s} = \frac{I_{SERS}}{I_{RS}} \frac{H_{eff} \times \rho_v}{\rho_s}$$

where

- I_{RS} is the signal-to-base Raman intensity of the analyte molecules

under non-SERS conditions which in our case is R6G powder on a glass slide and I_{SERS} the intensity under SERS conditions.

- D is the diameter of the excitation spot of the objective;
- H_{eff} [μm] is the diameter of the excitation spot of the objective, which is measured as $\sim 100 \mu\text{m}$ for the $20\times$ objective;³
- ρ_v [$\text{mol}/\mu\text{m}^3$] is the volume density of the pure R6G powder. As the mass density of R6G powder is $1.26 \text{ g}/\text{cm}^3$ and the molecular weight of R6G is $479 \text{ g}/\text{mol}$, the ρ_v [$\text{mol}/\mu\text{m}^3$] = $(1.26/479) \times 10^{-12} = 2.63 \times 10^{-15} \text{ mol}/\mu\text{m}^3$;
- ρ_s [$\text{mol}/\mu\text{m}^2$] is the surface density of the R6G molecules adsorbed on the SERS substrate. The $4 \mu\text{L}$ droplet of 10^{-5} M R6G has $10^{-5} \times 4 \times 10^{-6} = 4 \times 10^{-11} \text{ mol}$ molecules. The droplet finally reduces to a contact area with a diameter $\sim 600 \mu\text{m}$. Thus, ρ_s [$\text{mol}/\mu\text{m}^2$] = $4 \times 10^{-11} / (\pi \times 600^2) = 3.54 \times 10^{-17} \text{ mol}/\mu\text{m}^2$

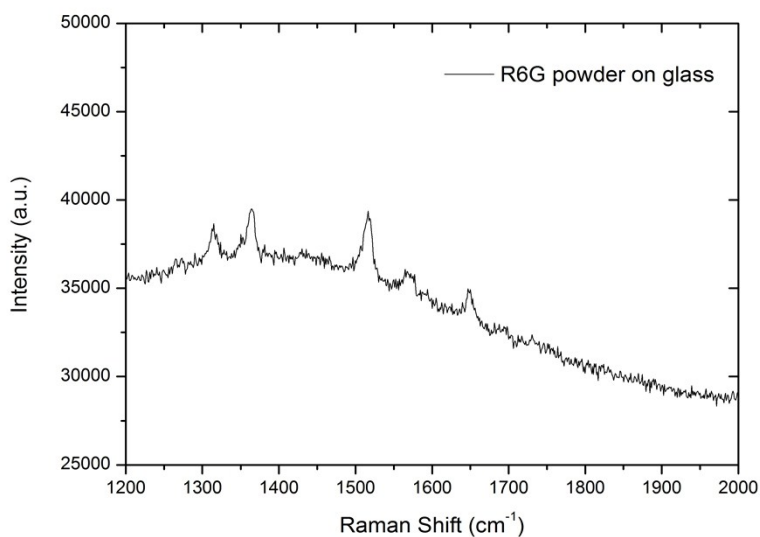


Figure S4. Raman spectrum of R6G powder on a glass slide

Therefore, for the 1363 cm^{-1} Raman peak, I_{RS} is ~ 2024 counts from Figure S4 above and I_{SERS} is ~ 3100 counts from Figure 4a in the manuscript. While for the 1643 cm^{-1} Raman peak, I_{RS} is ~ 414 counts and $I_{SERS} \sim 5000$ counts. The EFs can be calculated as:

$$EF(1363\text{ cm}^{-1}) = (3100/2024) \times (100 \times 2.63/3.54) \times (10^{-15}/10^{-17}) = 1.14 \times 10^4$$

$$EF(1643\text{ cm}^{-1}) = (5000/414) \times (100 \times 2.63/3.54) \times (10^{-15}/10^{-17}) = 0.90 \times 10^5$$

Reproducibility evaluation

The reproducibility is evaluated by calculating the Relative Standard Deviation (RSD), defined as the Standard Deviation divided by the mean of intensities of Raman peaks over the spectra collected. The RSD of signal-to-base intensity of

the 1363 cm^{-1} peak of the R6G is about 14.5% for all 1672 spectra in Figure S2 but reduces to 9.7% when the data of the dark region area are removed.

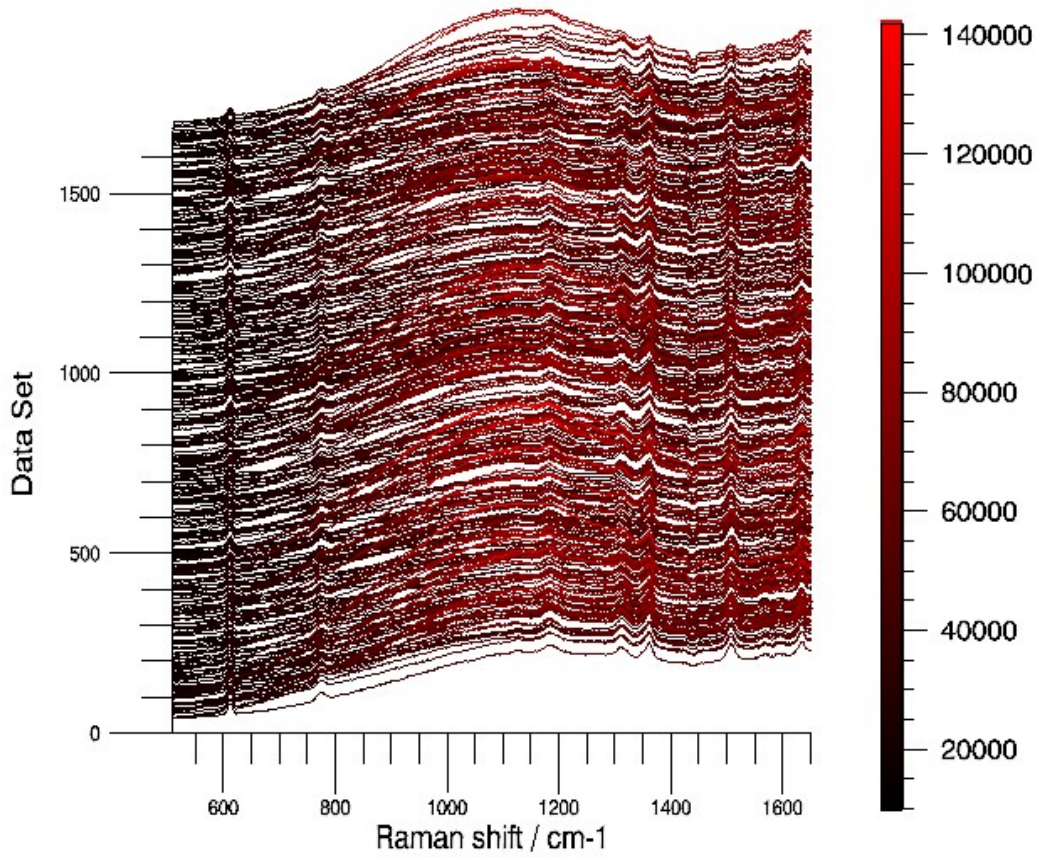


Figure S5. The 1672 R6G Raman spectra of measured by the mapping on a $120 \times 100 \mu\text{m}^2$ area of the Taro leaf@Ag sample.

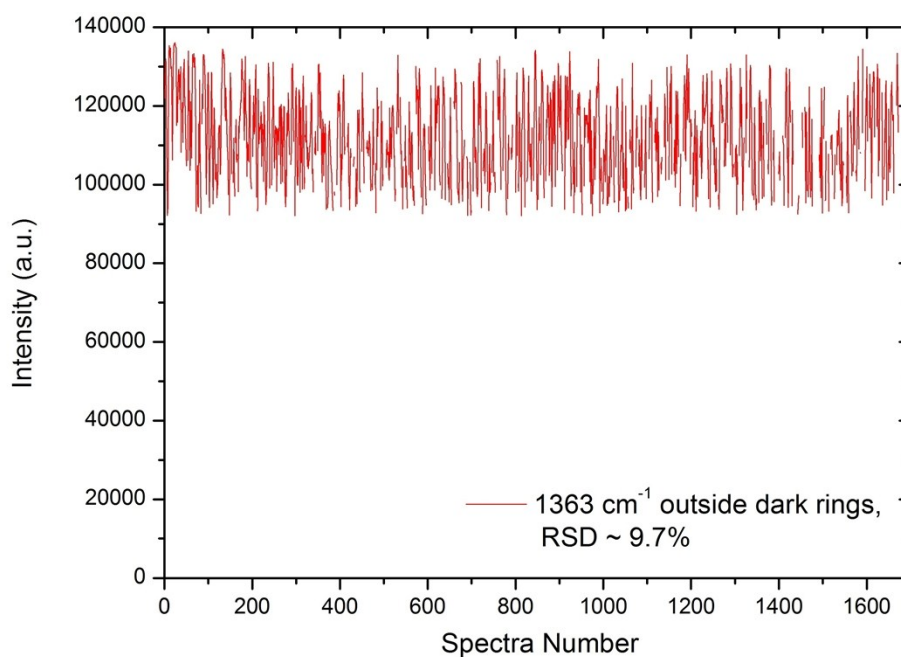
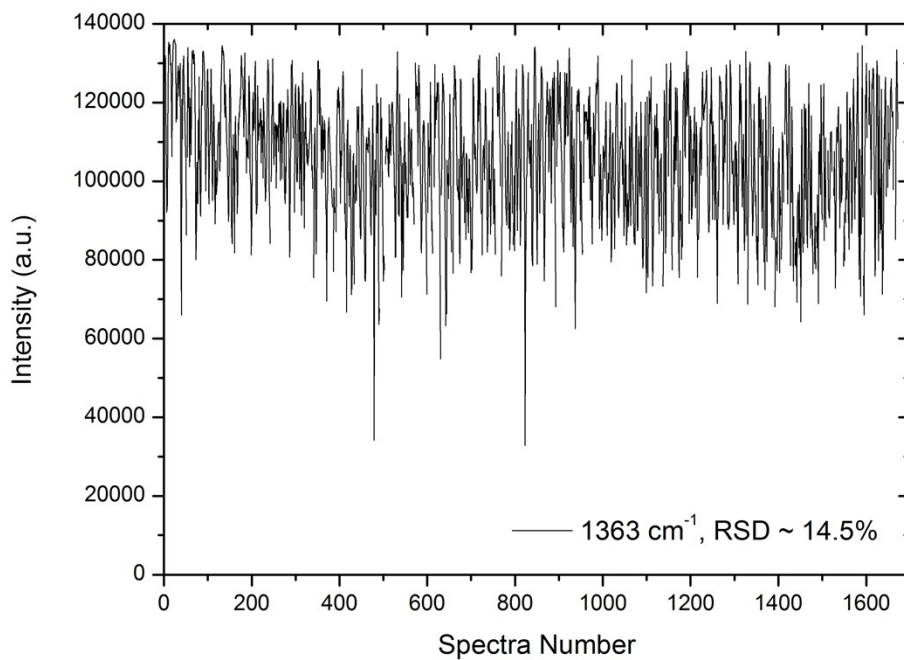


Figure S6. Signal intensity of the 1363 cm⁻¹ peak of (top) the 1672 R6G measured by the mapping and (bottom) the 1274 spectra in the mapping area outside the dark regions.

Reference

1. S. Wieckowski and G. Majewska, *Journal of Plant Physiology*, 1990, **136**, 701-704.

2. B. J. Murray, O. Li, J. T. Newberg, E. J. Menke, J. C. Hemminger and R. M. Penner, *Nano Letters*, 2005, **5**, 2319-2324.
3. E. Smith and G. Dent, *Modern Raman spectroscopy : a practical approach*, J. Wiley, Hoboken, NJ, 2005.