Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

A Highly-efficient, Stable and Flexible Kapton Tape-based SERS Chip

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Experiment Section

Materials. Rhodamine 6G (R6G, $C_{28}H_{31}N_2O_3Cl$, 99.9%) was purchased from Sigma-Aldrich. Tetramethylthiuram Disulfide (TMTD, $C_6H_{12}N_2S_4$, >98.0%) was purchased from TCI. Malachite Green (MG, $C_{23}H_{25}ClN_2$, >99.7%) was purchased from RHAWN Reagent, Company in Shanghai, China. Alcohol was obtained from Enox. N-type Si (<100>, 0.008-0.02 Ω·cm resistance) was bought from Suzhou Crystal Silicon Electronic (Suzhou) Technology Co., Ltd. The 5 mm*10 m Kapton tape was bought from SANJIA Company, China. The 3 M black electric tape (1712), the 8 mm*20 m carbon conductive double-faced adhesive tape (7311), the 3 M 25 mm*65 m transparent adhesive tape (Scotch 810 Tape), the Deli 60 mm*50 m transparent sealing tape, and apple were purchased from the local market. Ultrapure silver (Ag) particles (99.99%) were obtained from Zhong Nuo Advanced Material (Beijing) Technology Co., Ltd.

Characterizations. Sample morphology was characterized by using a Supera 55 Zeiss scanning electron microscope (SEM). A gold thin film (2 nm) was sputtered onto the tape to increase the conductivity of the surface before SEM characterization. The topography images of the samples were characterized using an atomic force microscopy (AFM) (Dimension Icon, Bruker) with a probe of SNL-10. SERS measurements were taken by an HR 800 Raman Spectroscopy (JY, France) with 633 nm laser and 100× objective. The acquisition time was 5s or 10 s and the max laser power was 5 mW. The nanogaps of nanoparticles were measured by Image J software.

Deposition of Ag on various substrates. Water contact angles (CAs) were measured on a CA system (OCA20, Dataphysics, Germany) at ambient temperature and the droplet volume was 3 µL. The Kapton tape with high surface energy was obtained by O_2 plasma treatment (PJ, AST, United States). The plasma treatment time was 10 s and the RF power was 250 W with pure O_2 (20 sccm) at a pressure of 0.35 Torr. After that, 50 nm Ag was directly evaporated on the Kapton tape, O_2 plasma-treated Kapton tape, and silicon wafer. Additionally, 50 nm Ag was also directly evaporated on other types of tape with different surface energies.

Fabrication of SERS chips. Firstly, after removing the protective polyethylene terephthalate (PET) film, Kapton tapes were adhered to a silicon wafer and put inside thermal evaporation equipment (OLED5, China). Subsequently, Ag film with different thicknesses including 40 nm, 60 nm, 80 nm, 100 nm, 120 nm and 140 nm were directly evaporated on the tape surfaces at 0.30 ± 0.10 Å/s under the chamber pressure of 10^{-4}–10^{-5} Pa respectively.

SERS measurements. R6G was chosen as a probe molecule to evaluate the SERS performance of the chips. 5 µl R6G ethanol solution with different concentrations were dropped on various substrates and left to naturally dry, respectively. Afterward, SERS spectra were collected using 5 µW laser power and 10 s acquisition time.

Calculation of enhancement factor (EF). The enhancement factor (EF) was calculated according to the following equation:

$$EF = \frac{I_{SERS} N_{bulk}}{I_{bulk} N_{surf}} \quad (1)$$

In this equation, I_{SERS} is the SERS intensity of R6G (10^{-4} M) (I_{SERS}= 746338.78 a.u.mW^{-1}) absorbed on the AgNOT-80 chip, I_{bulk} is normal Raman intensity of bulk R6G (I_{bulk}=42.05 a.u.mW^{-1}) absorbed on a clean silicon wafer. The N_{surf} and N_{bulk} are the corresponding number of probe molecules in the laser spot area in SERS and normal Raman measurements, respectively. N_{surf} and N_{bulk} need to be calculated. N_{surf} can be calculated by:

$$N_{surf} = \left(\frac{N_A}{S_{sub}}\right) S_{laser} CV \quad (2)$$

where N_A is the Avogadro's number (6.02×10^{23}), C is the concentration of the R6G solution (10^{-4} M), V is the volume of the R6G solution (5 µL), S_{sub} is the solution surface area on substrate (4 mm in diameter), and S_{laser} is the size of the laser spot (2 µm in diameter). Therefore, N_{surf} was calculated to be about 7.53×10^7. N_{bulk}can be estimated by:

$$N_{bulk} = \frac{S_{laser} d\rho}{M} N_A \quad (3)$$

where d is the penetration depth (about 21 µm),[1] ρ is the density of solid R6G (1.3 g/cm^3), and M is the molar mass of R6G (479 g/mol). N_{bulk} was estimated to be about 1.08×10^{11}. Thus, the EF was estimated to be about 2.55×10^7.

Practical applications. The apples were cleaned thoroughly with ultrapure water. After drying, the apple peels were cut into 1×1 cm square. Then, 5 µl of different concentrations (6 µg/cm^2, 3 µg/cm^2, 0.6 µg/cm^2, 0.3 µg/cm^2, 0.06 µg/cm^2) TMTD ethanol solution were spread on the clean apple peels and dried at room temperature, respectively. Subsequently, the SERS chip was gently pasted on the peel, held for a

few seconds, and then slowly peeled off for SERS analysis. The SERS spectra were acquired using 50 μW laser power and 10 s acquisition time. In addition, 0.6 μg/cm^2 of TMTD and MG mixed solution was tested in the same way.

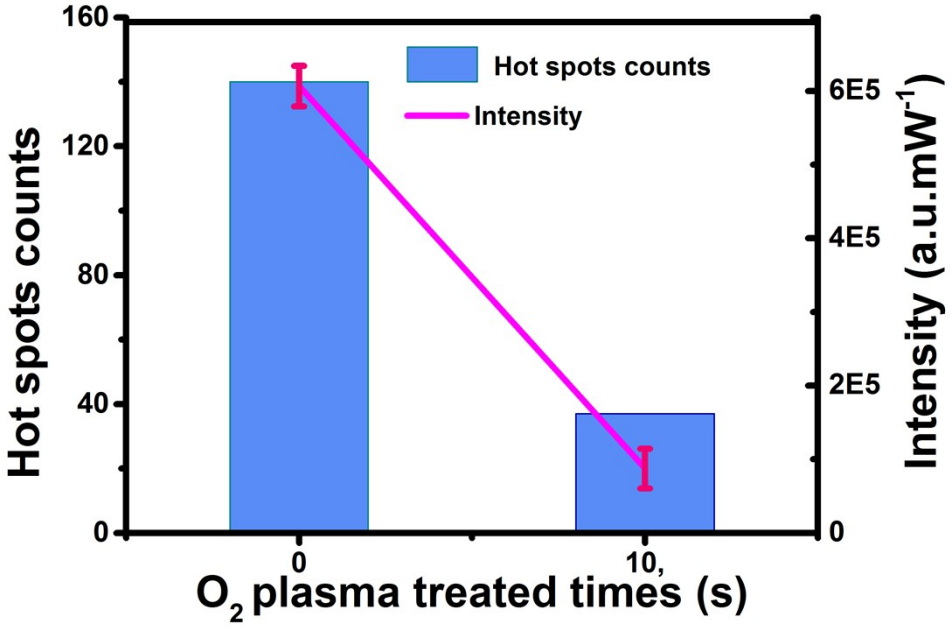

Figure S1. The correlation among the hot spots counts, SERS intensities of R6G at 1511 cm^{-1} and the O_2 plasma treated times.

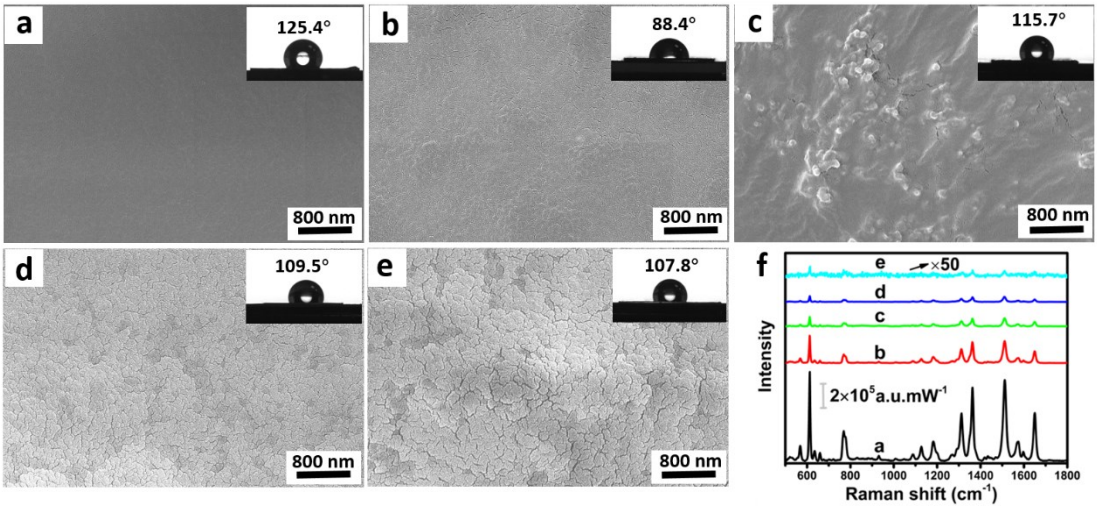

Figure S2. SEM images of various tapes: (a) Kapton tape, (b) 3 M black electric tape, (c) Carbon conductive double-faced adhesive tape, (d) 3 M adhesive tape, and (e) Deli transparent sealing. The inset was 3 ul water droplet on each tape. (f) SERS spectra of 10^{-4} M R6G dropped on corresponding tapes after 50 nm Ag directly evaporated.

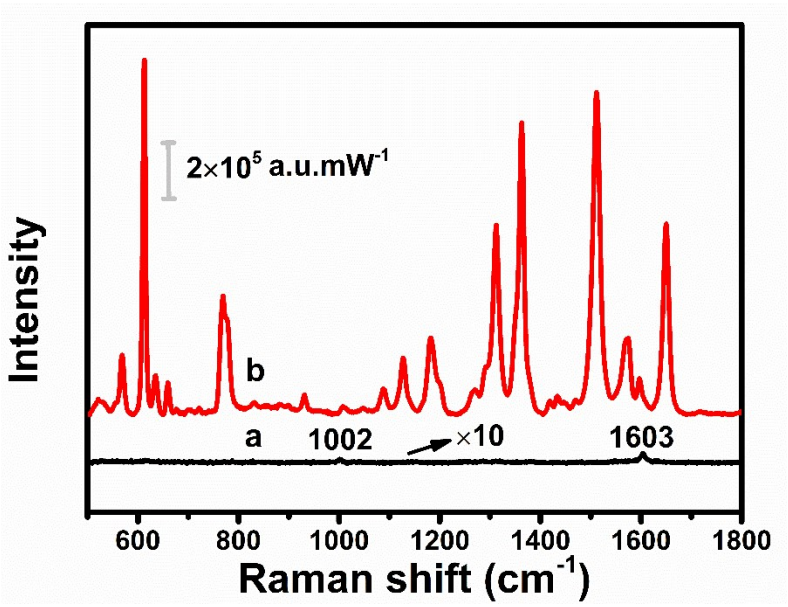

Figure S3. (a) Raman spectra of bare AgNOT chip. (b) SERS spectra of 10^{-4} M R6G dropped on the AgNOT chip.

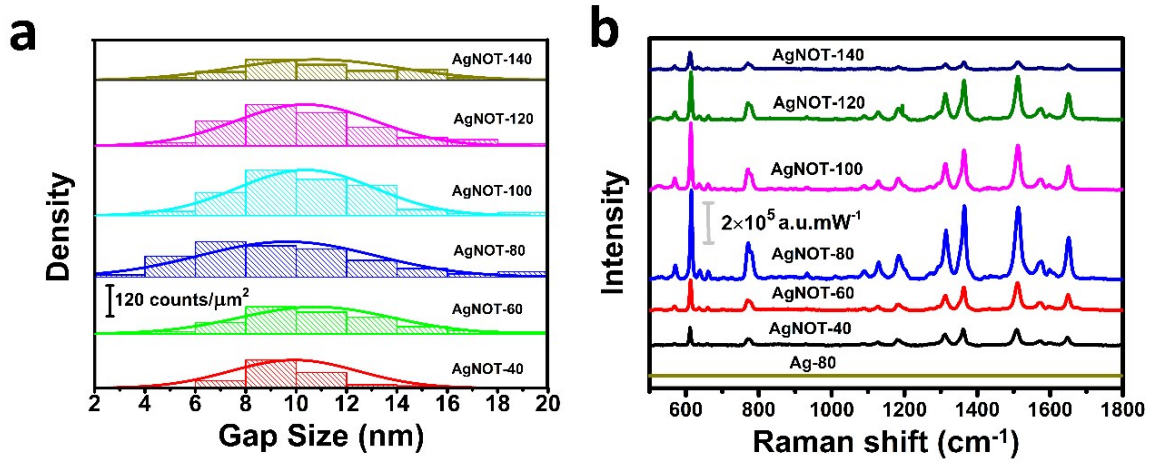

Figure S4. (a) The gap size density in randomly selected 500 nm × 500 nm area from the AgNOT-40, 60, 80, 100, 120, and 140 chips. (b) SERS spectra of 10^{-5} M R6G dropped on the AgNOT-40, 60, 80, 100, 120, and 140 chips.

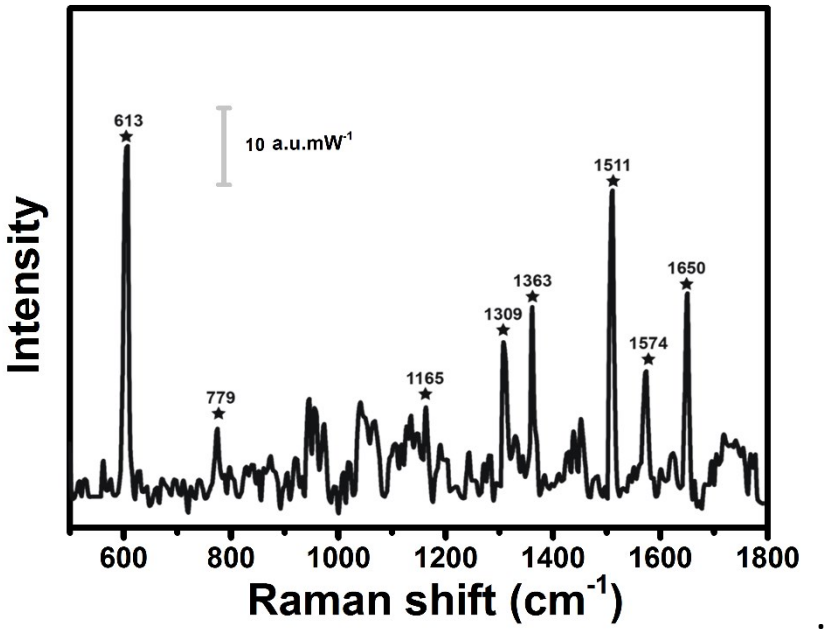

Figure S5. Raman spectrum of R6G solid powder.

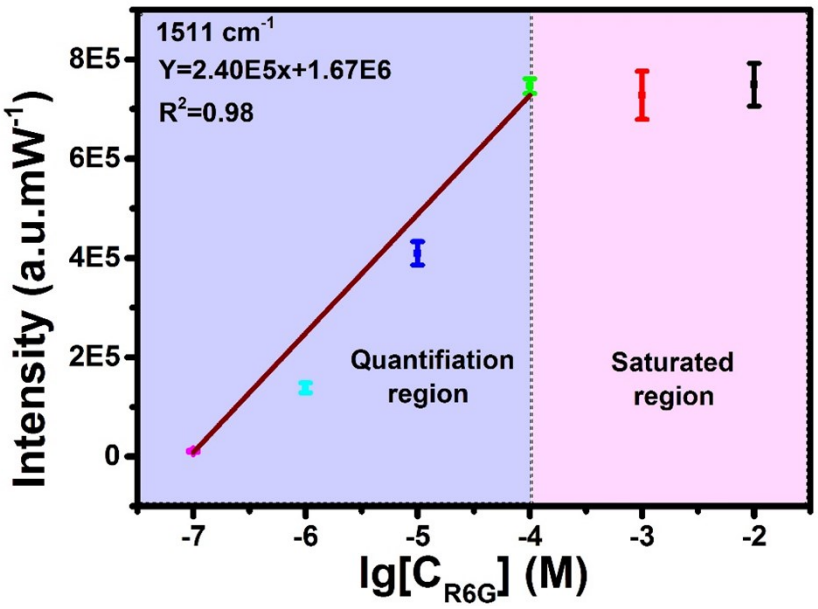

Figure S6. The correlation between the SERS intensities of R6G at 1511 cm^{-1} and the logarithm of R6G concentration.

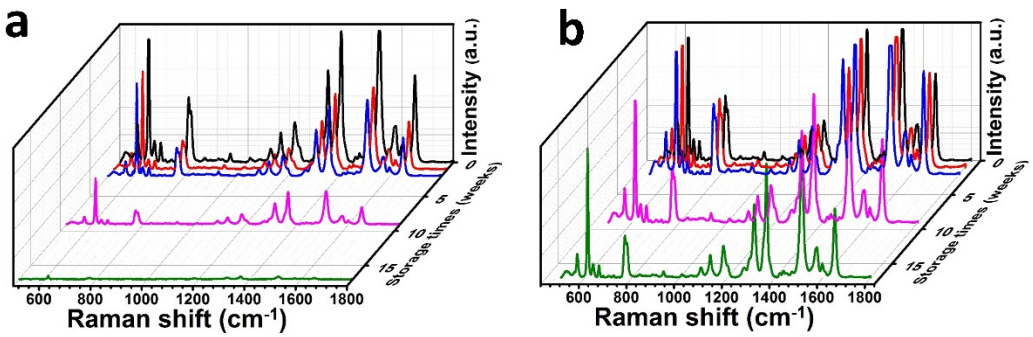

Figure S7. SERS spectra of 10^{-4} M R6G enhanced by the AgNOT-80 chip at different storage times of 0, 1, 2, 9, and 17 weeks: (a) without PET film, (b) with PET film.

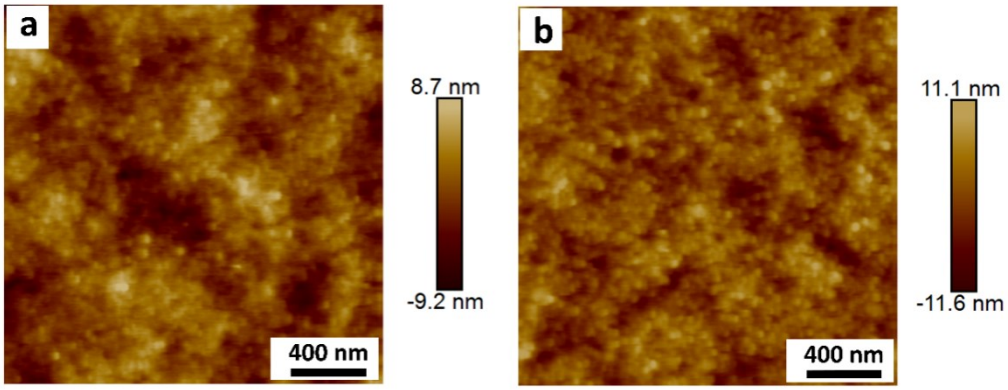

Figure S8. AFM topography images of (a) the AgNOT-80 chip, (b) the AgNOT-80 chip after the PET film packaging and peeling off.

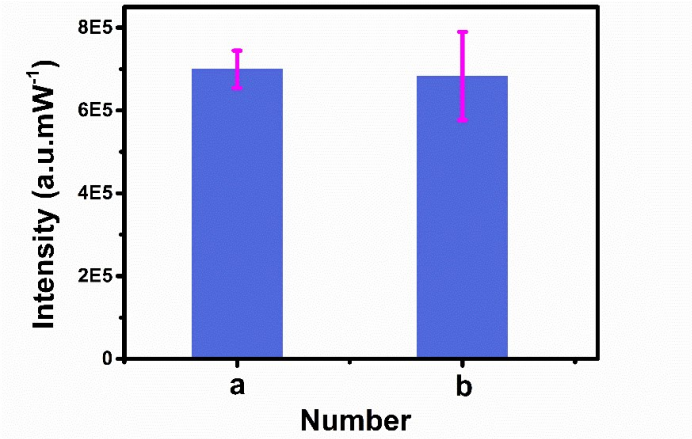

Figure S9. SERS intensities of 10^{-4} M R6G at 1511 cm^{-1} enhanced by the AgNOT-80 chip: (a) without thermal annealing. (b) after annealing in air at temperatures of 100 °C for 1 hour through a heating plate.

References

1. W. B. Cai, B. Ren, X. Q. Li, C. X. She, F. M. Liu, X. W. Cai and Z. Q. Tian, Investigation of surface-enhanced Raman scattering from platinum electrodes using a confocal Raman microscope: dependence of surface roughening pretreatment, *Surf Sci*, 1998, **406**, 9-22.