

Electronic Supplementary Material (ESI)

**Nanoscale tracking plasmon-driven photocatalysis in
individual nanocavities by vibrational spectroscopy**

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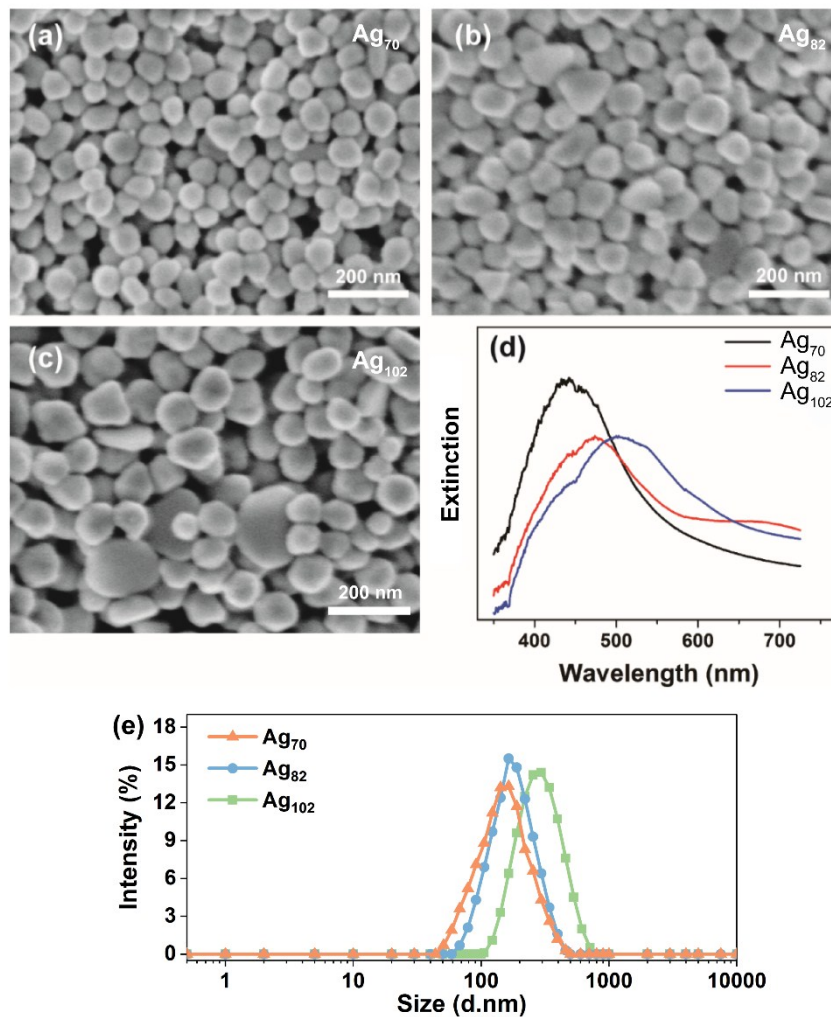


Fig. S1 SEM images of the Ag NPs with average diameters of about (a) 70 nm, (b) 82 nm and (c) 102 nm. (d) UV/visible extinction spectra of the three corresponding kinds of Ag NPs shown in (a), (b) and (c). (e) The mean hydration diameters the three Ag NPs are measured to be 87.2 nm, 137.2 nm and 223.1 nm, respectively.

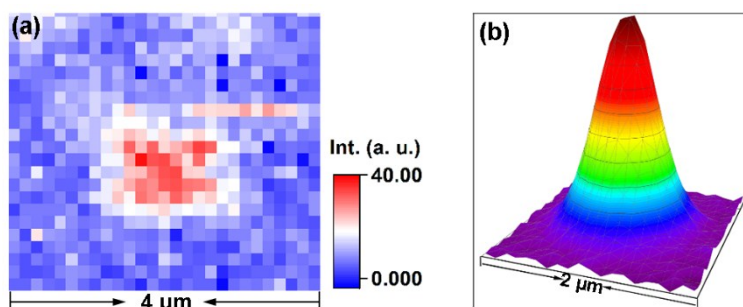


Fig. S2 (a) SERS mapping of a single Ag NP dispersed on the Au mirror using the 1342 cm^{-1} band

intensity of 4-NTP, (b) Three-dimensional representation of the image in (a) (638 nm excitation laser, 0.24 mW laser power, 1 s integration time).

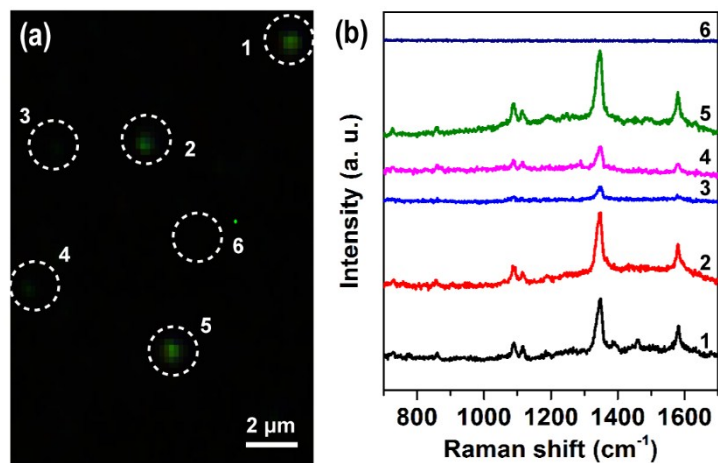


Fig. S3 (a) DF image of the Ag NPs deposited on the Au TF surface. (b) SERS spectra recorded from the corresponding locations labeled in (a).

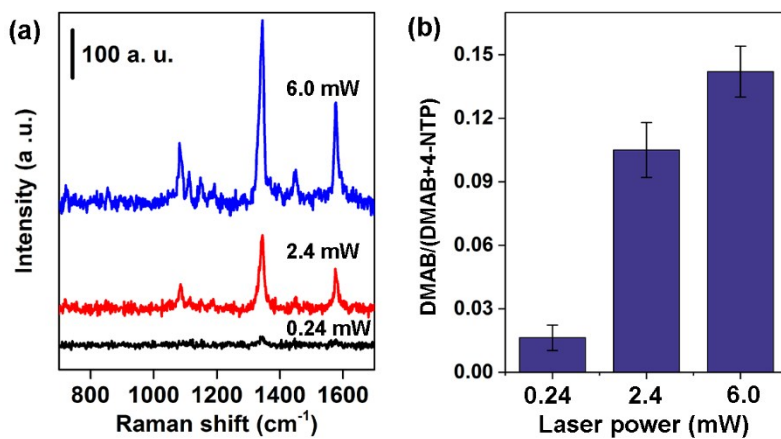


Fig. S4 (a) SERS spectra obtained with the excitation of different laser powers (638 nm, 1 s integration time). (b) Intensity ratios of the peak at 1146 cm⁻¹ to the peak at 1342 cm⁻¹ as a function of the laser power.

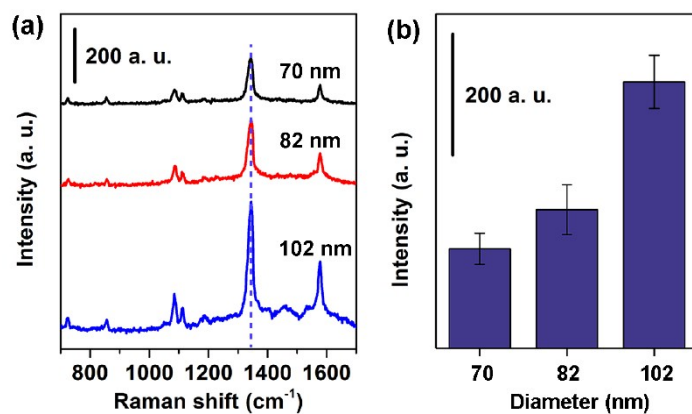


Fig. S5 (a) SERS spectra obtained from individual Ag NPoM junctions constructed with 70 nm, 82 nm, and 102 nm Ag NPs, respectively. (b) The 1342 cm^{-1} Band intensities of the corresponding spectra shown in (a). The error bar represents the average of three measurement.