Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

Plasmon-Driven Protodeboronation Reactions in Nanogaps

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1. List of Materials and Instruments

Materials

4- Mercaptophenylboronic acid (MPBA, 90 %, Sigma-Aldrich)
Benzenethiol (BT, ≥ 99 %, Sigma-Aldrich)
AuNPs (51 ± 13 nm, bare surfaces, Cytodiagnostics)
Au substrates (150 nm thick film on Si or 50 nm thick film on glass slides, e-beam evaporation, National Nanofab Center, Daejeon, Korea)
Water (HPLC grade, J. T. Baker)
Ethyl alcohol (99.9 %, Samchun Chemical)
Sodium metaborate tetrahydrate (≥ 99 %, Sigma-Aldrich)
Boric acid (≥ 99.5 %, Sigma-Aldrich)
Zero air (O_2 21% / N_2, 99.995 %, Dae-Deok Gas)
Argon (Ar, 99.999 %, AirKorea)
Oxygen (O_2, 99.995 %, Deokyang)

Instruments

Lasers:
- 785 nm laser (Invictus, Kaiser Optical Systems)
- 638 nm laser (06-MLD, 633 nm, Cobolt)
- 532 nm laser (Excelsior-532, Spectra Physics)
- Laser power meter (PM100D, Thorlabs)

Raman spectroscopy:
- Microscope (DM, Leica) with 50× objective (Leica N.A 0.75) or 10× objective (Leica N.A. 0.25)
- Spectrometer (resolution 5 cm^{-1}, RamanRxn1, Kaiser Optical Systems)

Heating:
- Infrared thermometer (561, Fluke)
- Heater (18 W, ELT-2018, Exso)

For dark-field single-particle scattering spectroscopy:
- Microscope (IX-73, Olympus)
- Halogen lamp (Olympus)
- Oil-immersion type dark-field condenser (N.A. 1.2-1.4, U-DCW, Olympus)
- 100× objective (Olympus, N.A. 0.90)
- CCD imaging camera (Infinity 2-1R, Lumenera)
- Spectrometer (focal length 320 mm, f/4.2, MonoRa320i, Dongwoo Optron) with CCD (iDus, Andor)

Scanning electron microscope (SEM, Sigma, Carl Zeiss)

2. Distribution of AuNPs on MPBA SAMs on Au Substrates

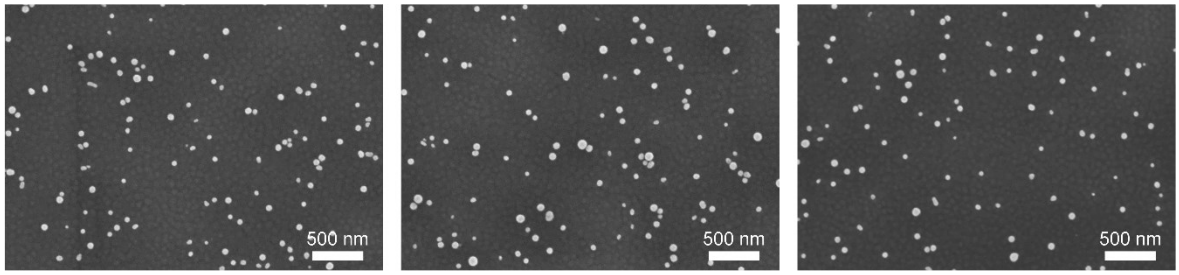

Figure S1. Representative SEM images of AuNPs on the MPBA SAMs. The average number of AuNPs within a 10 μm circular area is approximately 870.

3. SERS Spectra of MPBA at Lower Raman Excitation Laser Power

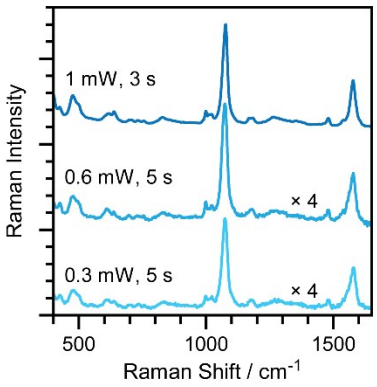

Figure S2. Representative SERS spectra of MPBA SAMs between AuNPs and Au substrates, acquired at Raman excitation laser powers of 0.3, 0.6, and 1 mW. The exposure time was 3 or 5 s, as indicated. The spectra were offset for clarity. The small vibrational peak at 998 cm^{-1} is still visible at low laser power, suggesting that the peak observed prior to plasmon excitation laser irradiation in Figures 2, 3, and 6 is not from the deboronation reaction induced by the Raman excitation laser, but rather the inherent vibrational feature of MPBA.

4. Kinetics

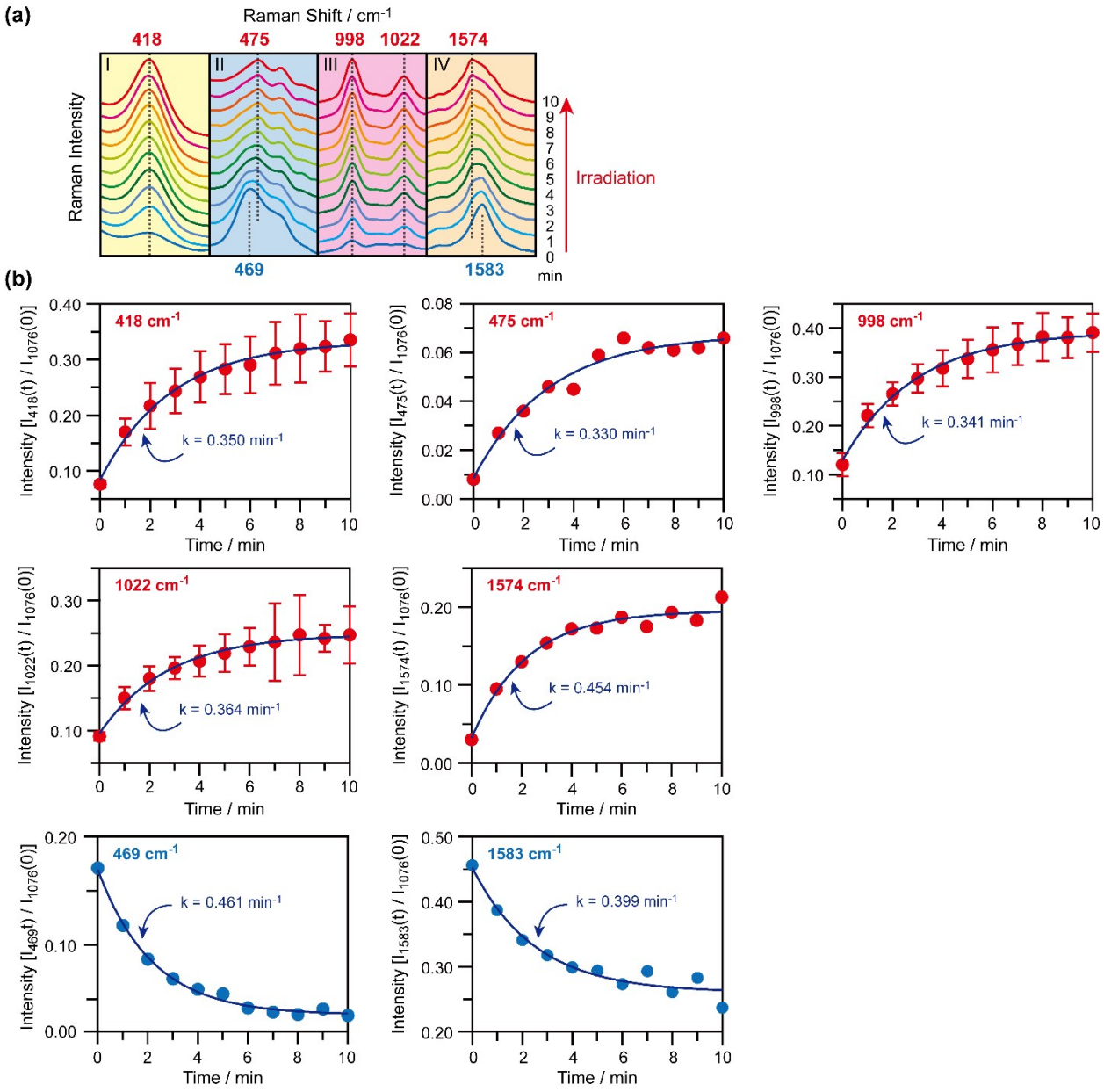

Figure S3. Change in the SERS peak intensity of the MPBA SAMs in the NPoM nanogaps with increasing irradiation time at 785 nm. The peaks corresponding to the BT product (labeled in red) rise at almost the same rate as the peaks corresponding to the MPBA reactant (labeled in blue) decay.

5. Reproduction of Spectrum Using the Reaction Yield

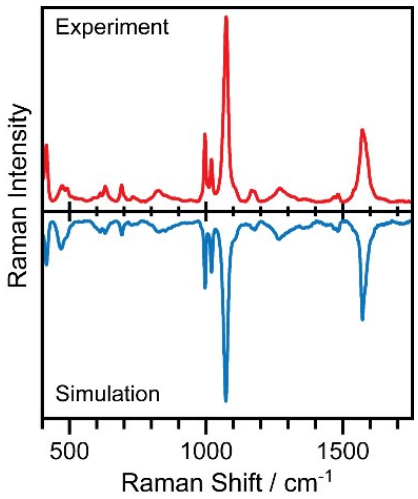

Figure S4. (Top panel) Experimental SERS spectrum of the MPBA SAMs in NPoM, acquired after irradiation at 785 nm for 10 min. (Bottom panel) Simulated spectrum obtained by adding (Y × BT spectrum) and ((1–Y) × MPBA spectrum), where Y is the reaction yield, and the BT and MPBA spectra are normalized with respect to the 1076 cm^{-1} peak that commonly appears in both spectra. The reaction yield, Y = 0.34, gives the best result as shown above.

6. Evidence for the Laser-Induced Protodeboronation Reaction

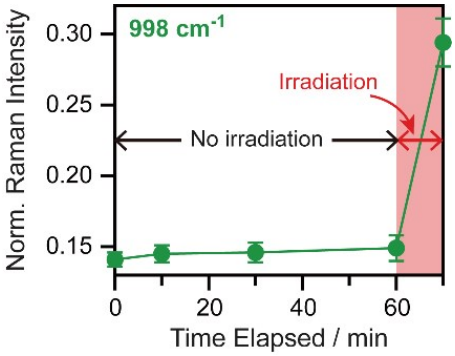

Figure S5. Normalized Raman peak intensity at 998 cm^{-1} that corresponds to the BT product as the sample is left idle for 60 min and then irradiated at 785 nm for 10 min.

7. Dark-Field Single-Particle Scattering Spectra

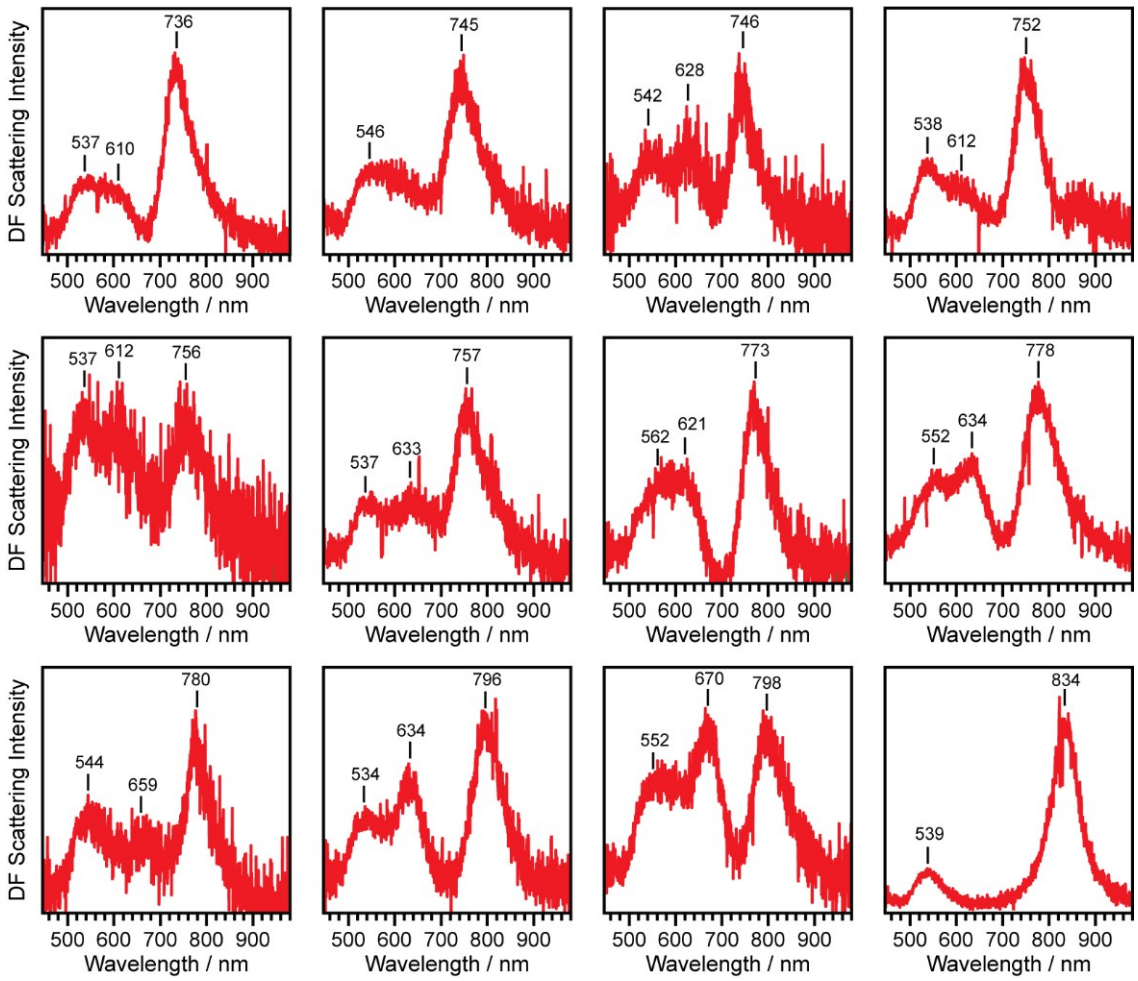

Figure S6. Collection of dark-field single-particle scattering spectra acquired for individual AuNPs on the MPBA SAMs on the Au film.

8. Detection of Metaboric Acid

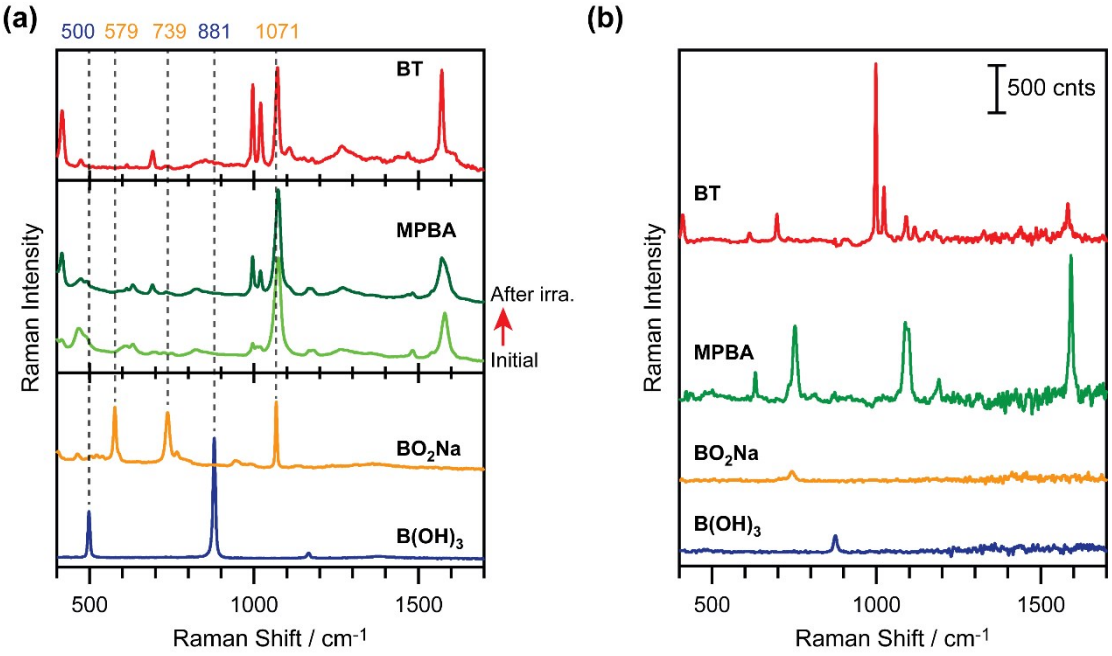

Figure S7. Attempts to detect the other product, metaboric acid (OH–B=O). Protodeboronation of MPBA produces BT and metaboric acid. We attempted to detect the metaboric acid as well as MPBA using SERS. (a) Raman spectra of sodium metaborate ($NaBO_2$) and boric acid ($B(OH)_3$) in solids (bottom panel). No evident peaks assignable to metaborate or boric acid were found in the SERS spectrum of MPBA after irradiation at 785 nm for 10 min (middle panel). (b) Raman spectra of BT, MPBA, metaborate, and boric acid in 1 M solution, obtained under the same conditions. Solvent spectra were subtracted. Raman scattering cross-sections of metaborate and boric acid are much smaller than those of the aromatic compounds, such as MPBA and BT.