

Electronic Supplementary Information

Surface-Enhanced Raman Scattering of 4-Aminobenzenethiol on Gold: The Concept of Threshold Energy in Charge Transfer Enhancement

Kwan Kim,^{*a} Dongha Shin,^a Hyang Bong Lee,^a and Kuan Soo Shin^{*b}

^a*Department of Chemistry, Seoul National University, Seoul 151-742, Korea. E-mail:*

kwankim@snu.ac.kr; Fax: +82 2 889 1568; Tel: +82 2 880 6651

^b*Department of Chemistry, Soongsil University, Seoul 156-743, Korea. E-mail:*

kshin@ssu.ac.kr; Fax: +82 2 824 4383; Tel: +82 2 820 0436

EXPERIMENTAL SECTION

Benzenethiol (BT), 4-Aminobenzenethiol (4-ABT), 4-nitrobenzenethiol (4-NBT), sodium borohydride (99%), and gold wire (99.999%) were purchased from Aldrich and used as received. All chemicals unless specified were of reagent grade, and triply distilled water of resistivity greater than 18.0 M Ω -cm was used throughout.

Two different gold substrates were used in this work. One is an electrochemically roughened Au wire and the other consists of vacuum-evaporated Au film on mica. Specifically, the Au wire was roughened electrochemically in 0.1 M KCl solution by cycling between -0.8 V and +1.0 V. On the other hand, the Au island films were prepared by resistive evaporation of gold at 10⁻⁶ Torr onto a freshly cleaved mica substrate. The adsorption of BT, 4-NBT and 4-ABT on Au was performed by immersing the Au substrate in a 0.1 mM ethanolic solution overnight.

Raman spectra were obtained using a Renishaw Raman system Model 2000 spectrometer equipped with an integral microscope (Olympus BH2-UMA). Unless stated, the 632.8 nm line from a 17 mW He/Ne laser (Spectra Physics Model 127) was used as the excitation source. The Raman band of a silicon wafer at 520 cm⁻¹ was used to calibrate the spectrometer, and the accuracy of the spectral measurement was estimated to be better than 1 cm⁻¹. Temperature-controlled experiments were conducted using a hot stage controlled by a Mettler Toledo FP90 Central Processor.

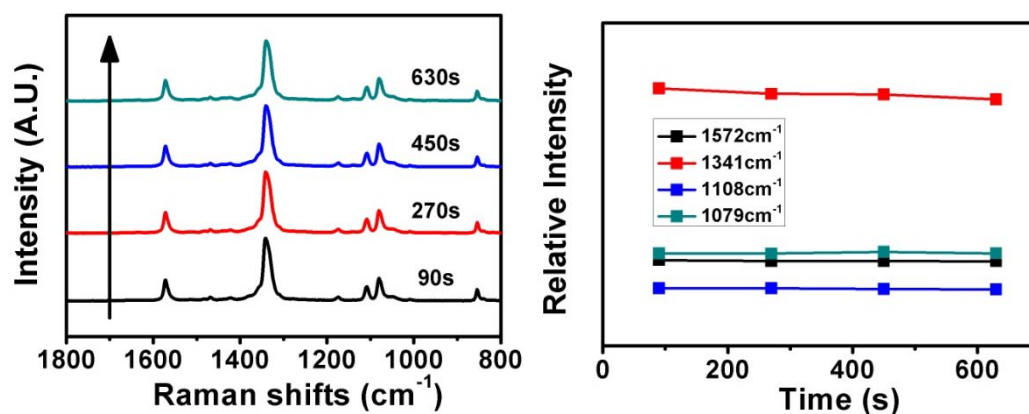


Fig. S1. Time series SERS spectra of 4-NBT on a vacuum evaporated Au film measured at a fixed power of 2.15 mW at the sampling position.

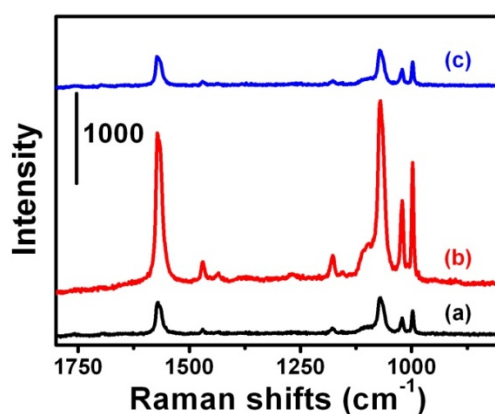


Fig. S2. Raman spectra of BT on a vacuum evaporated gold film recorded consecutively at a fixed point at the laser power of (a) level 1, (b) level 5, and then (c) back at level 1.