Electronic Supplementary Information

Effect of Polar Organic Vapors on Surface Potential of Au Nanoparticle Aggregates Probed By Surface-Enhanced Raman Scattering of 2,6-Dimethylphenylisocyanide

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Experimental details:

Hydrogen tetrachloroaurate ($HAuCl_4$, 99.99%), silver nitrate ($AgNO_3$, 99.99%), 2,6-dimethylphenylisocyanide (2,6-DMPI, 96%), dodecanethiol (98%), sodium perchlorate ($NaClO_4$, 98%), Au wire (99.9%), Ag wire (99.99%), and Pt wire (99.99%) were purchased from Aldrich, and used as received. Unless specified, other chemicals were reagent grade, and highly pure water whose resistivity is greater than 18.0 MΩ·cm was used throughout.

Aqueous Au sol was prepared following the recipes of Link et al.[1] Initially, 95 mL of aqueous $HAuCl_4$ solution containing 5 mg of Au was brought to the boil, and 5 mL of 1% sodium citrate was added therein under vigorous stirring, and boiling was continued for ~30 min. On the other hand, the Ag sol was prepared by following the recipes of Lee and Meisel.[2] Initially, 45 mg of $AgNO_3$ was dissolved in 250 mL of water, and the solution was brought to the boil. A solution of 1% sodium citrate (5 mL) was then added to the $AgNO_3$ solution under vigorous stirring, and boiling was continued for ~30 min. The Au and Ag sol then showed distinct surface plasmon bands at 520 and 400 nm, respectively, in the UV-vis spectra, and according to the transmission electron microscopy (TEM) analysis, both nanoparticles were spherical with a mean diameter of ~35 nm.

The Au(Ag) film was prepared by dropping 15 μL of Au(Ag) sol onto a mica substrate (1 mm × 30 mm). The injected mica substrate was left to dry under ambient conditions to form an Au(Ag) nanoaggregate film. After a thorough wash with water and drying in N_2 atmosphere, the film was immersed in 1 mM ethanolic solution of 2,6-DMPI for 1 h. After thorough washing with ethanol and drying, the 2,6-DMPI-adsorbed Au(Ag) film was inserted into a glass capillary (1.2 mm in inner diameter and 75 mm in length), and then subjected to Raman spectral analysis under the flow of organic vapors.

For potential-dependent SERS measurements, Au(Ag) wire was roughened electrochemically in 0.1 M KCl solution by cycling between -0.8 V and +1.0 V(-0.4 V and +0.8 V) and then immersed in 1 mM ethanolic solution of 2,6-DMPI for 1 h. The modified Au(Ag) wire and a pure Pt wire were used as a working and counter electrodes, respectively, in 0.1 M $NaClO_4$ solution. The potential of the electrochemical cell was controlled by using a CH Instruments model 660A potentiostat, which employed CHI 660A electrochemical analyzer software (version 2.03) running on an IBM-compatible PC. All potentials are reported with respect to the Ag/AgCl electrode.

UV-visible (UV-vis) spectra were obtained with a SCINCO S-4100 spectrometer. TEMs were obtained with a JEM-200CX transmission electron microscope at 200 kV after placing a drop of the as-prepared sol onto Ni/Cu grids. AFM images were obtained using a Digital Instrument model Nanoscope IIIa scanning probe microscope. Using a V-shaped, 200 μm long Si_3N_4 cantilever with a nominal spring constant of 0.12 N/m (Nanoprobe, Digital Instruments), topographic images were recorded in the conventional height mode (tapping mode, normal AFM) at a scan rate of 1 ~ 2 Hz. Raman spectra were obtained using a Renishaw Raman system Model 2000 spectrometer equipped with an integral microscope (Olympus BH2-UMA). 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}.

References

1 S. Link, Z. L. Wang and M. A. Elsayed., *J. Phys. Chem. B*, 1999, **103**, 3529.
2 P. C. Lee and D. Meisel., *J. Phys. Chem.*, 1982, **86**, 339

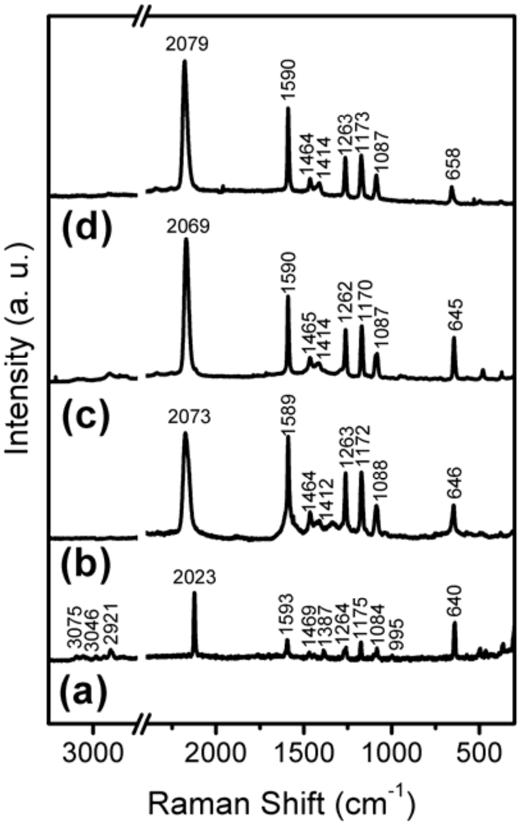

Fig. S1. (a) Normal Raman spectrum of 2,6-DMPI in neat state and its SERS spectrum (b) on Ag nanoparticle aggregates on a mica substrate, (c) in Ag sol, and (d) in Au sol.

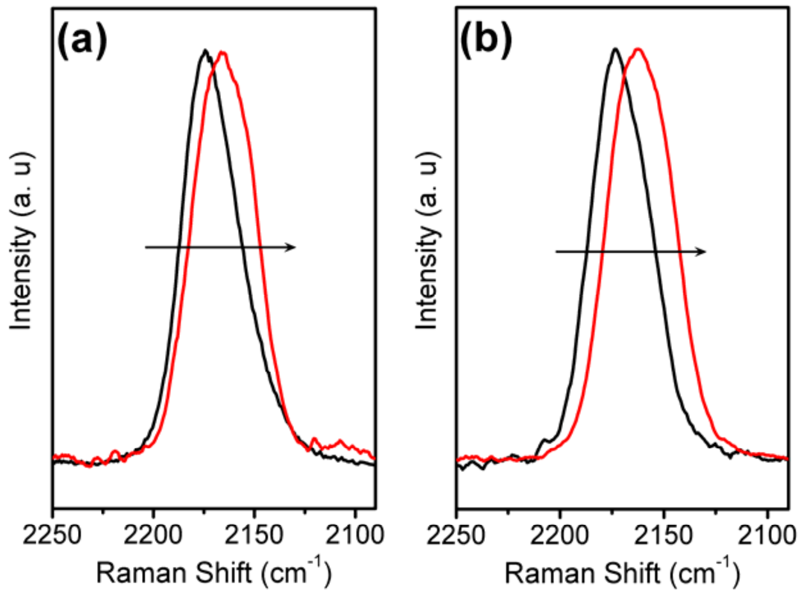

Fig. S2. Raman spectra taken under the flow of (a) acetone and (b) ammonia vapor over 2,6-DMPI-adsorbed Ag nanoparticle aggregates on a mica substrate put in a glass capillary. See Scheme 1 in the text.

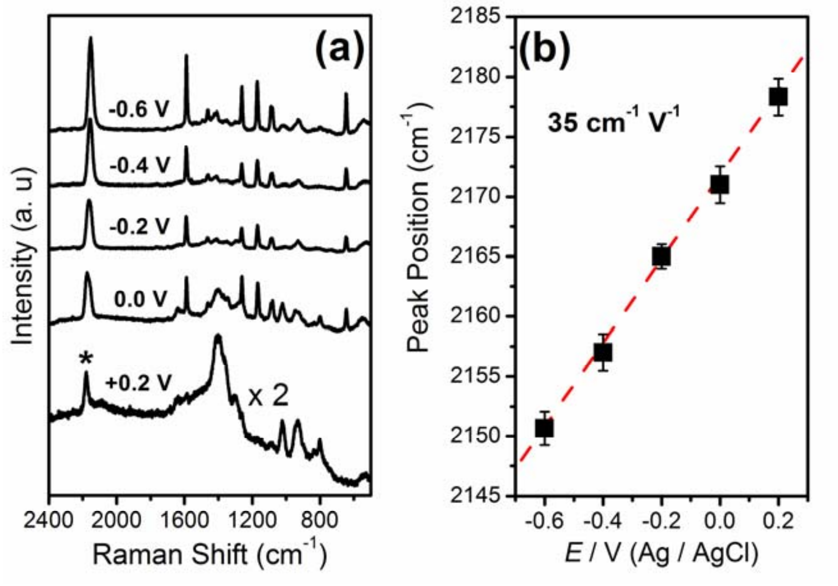

Fig. S3. (a) Potential-dependent SERS spectra of 2,6-DMPI on an Ag wire electrode in 0.1 M $NaClO_4$ aqueous solution. (b) Position of the NC stretching peak of 2,6-DMPI on Ag drawn versus the applied potential in (a).

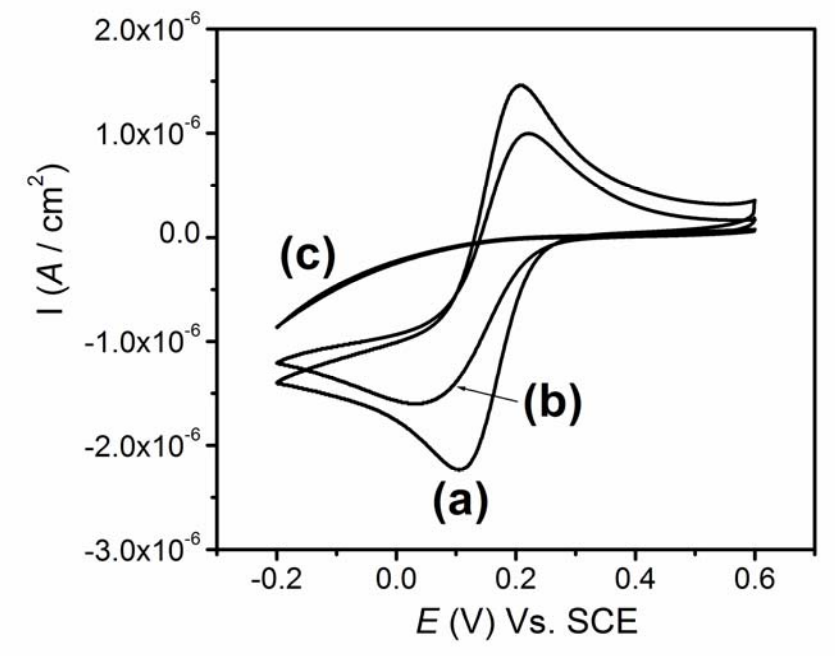

Fig. S4. Cyclic voltammograms of ferricyanide measured at a scan rate of 20 mV/s on (a) bare Au, (b) 2,6-DMPI-adsorbed Au, and (c) dodecanethiol-adsorbed Au electrodes in an aqueous solution containing 0.1 M KCl and 1 mM $K_3Fe(CN)_6$.