

Supporting Information

Subnanoscale Probing of Nanojunction using Heterogeneous Gap-Mode Raman Spectroscopy

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Experimental Section

Synthesis and characterization

Ag wire (0.25 mm diam., 99.95%), chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, 37.50% Pt basis), sodium citrate (99.9%), sodium borohydride (99%), L-ascorbic acid (99%), and 1,4-phenylene diisocyanide (1,4-PDI, 97%) were purchased from Aldrich and used as received. Other chemicals, unless specified, were reagent grade. Triply distilled water with a resistivity ($>18.2 \text{ M}\Omega \cdot \text{cm}$) was used for the synthesis of all aqueous solutions.

For smooth Ag surface, Ag wire was treated by flame annealing. After cooling down to room temperature, it was dipped in 1 mM ethanolic 1,4-PDI solution for 3 h, which were then washed thoroughly with ethanol to remove any physisorbed or excess 1,4-PDI molecules. A smooth Pt substrate (0.1 mm thick, 99.99%, Aldrich) was polished to a mirror finish using $0.05 \mu\text{m}$ alumina powder and then sonicated sequentially in isopropyl alcohol, hot piranha solution, and water.

Ag sol ($\sim 60 \text{ nm}$ diameter) was prepared according to the conventional Lee and Meisel method. Platinum sols ($\sim 100 \text{ nm}$) were prepared according to the recently developed novel seed-mediated growth method reported by Bigall *et al.* (reference 19 in the main text) Small platinum seeds with a diameter of $5\text{--}7 \text{ nm}$ were prepared initially, which then used for the synthesis of 26 nm Pt nanoparticles. These 26 nm Pt particles were used as seeds to prepare larger Pt particles. After the synthesis, the products were centrifuged at $1000\text{--}13500 \text{ rpm}$, then washed more than three times with DI water and stored in water. The particle size was characterized by transmission electron microscope (TEM, JEM-200CX, 160 kV).

To attach Pt nanoparticles onto the pendent NC groups of 1,4-PDI on Ag, the 1,4-PDI-adsorbed Ag substrate was soaked in Pt sol for 3 h. After washing thoroughly with water and ethanol, substrates were left to dry under ambient condition, then subjected to Raman spectral analyses.

In all cyclic voltammetry (CV) experiments, we followed previous experimental conditions. (see the ref. 23 in the main text)

Measurements

Electrochemical potential dependent Raman measurements and cyclic voltammetry were conducted with three electrodes system (Pt wire as counter, $\text{Ag}|\text{AgCl}$ as reference, and gap-mode substrate as working electrode) and operated by commercial potentiostat (CHI 660) instrument.

Raman spectra were obtained using a Renishaw Raman system model 2000 spectrometer equipped with an integral microscope (Olympus BH2-UMA).

The 568 nm laser line from a 20 mW Ar^+/Kr^+ laser (Melles-Griot model 35KAP431) was used as the excitation source. Raman scattering was detected over 180° using a Peltier-cooled ($-70 \text{ }^\circ\text{C}$) charge-coupled device (CCD) camera (400×600 pixels). The laser beam was focused onto a spot approximately $1 \mu\text{m}$ in diameter with an objective microscope at a magnification of $50\times$ ($<1 \text{ mW}$ at sample position to avoid photobleaching). The data acquisition time was usually 30 s . The holographic grating (1800 grooves per mm) and the slit allowed the spectral resolution to be 1 cm^{-1} . 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} .

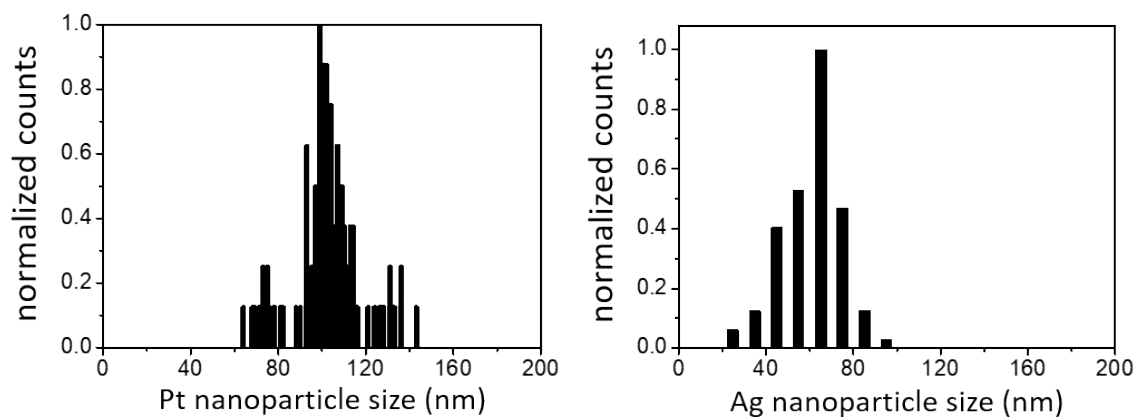


Figure S1. Size distribution of platinum (~100 nm) and silver (~60 nm) nanoparticles used in the experiments.

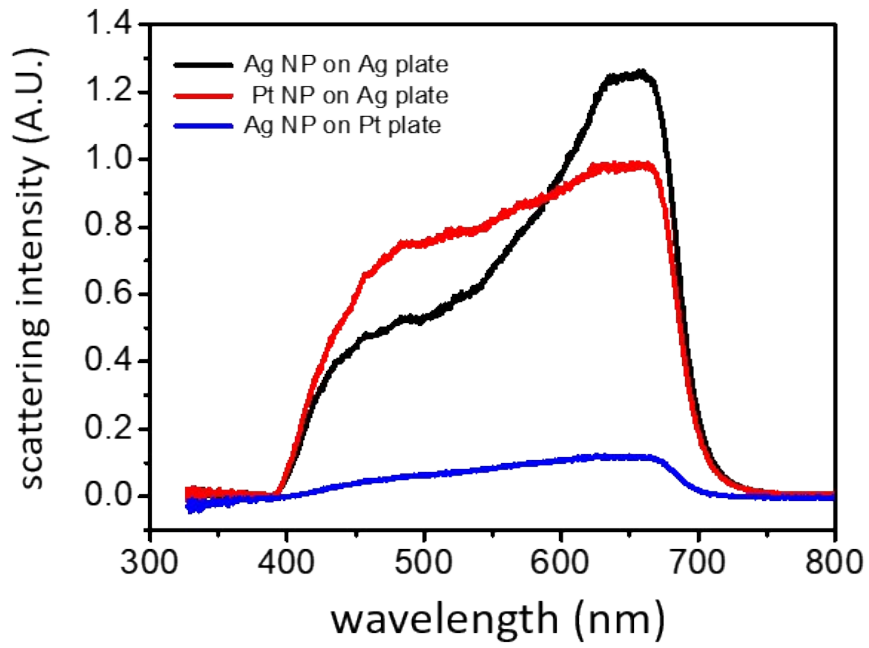


Figure S2. Dark field scattering spectra of three kinds of gap mode nanostructures, Ag NP on Ag plate, Pt NP on Ag plate and Ag NP on Pt plate.

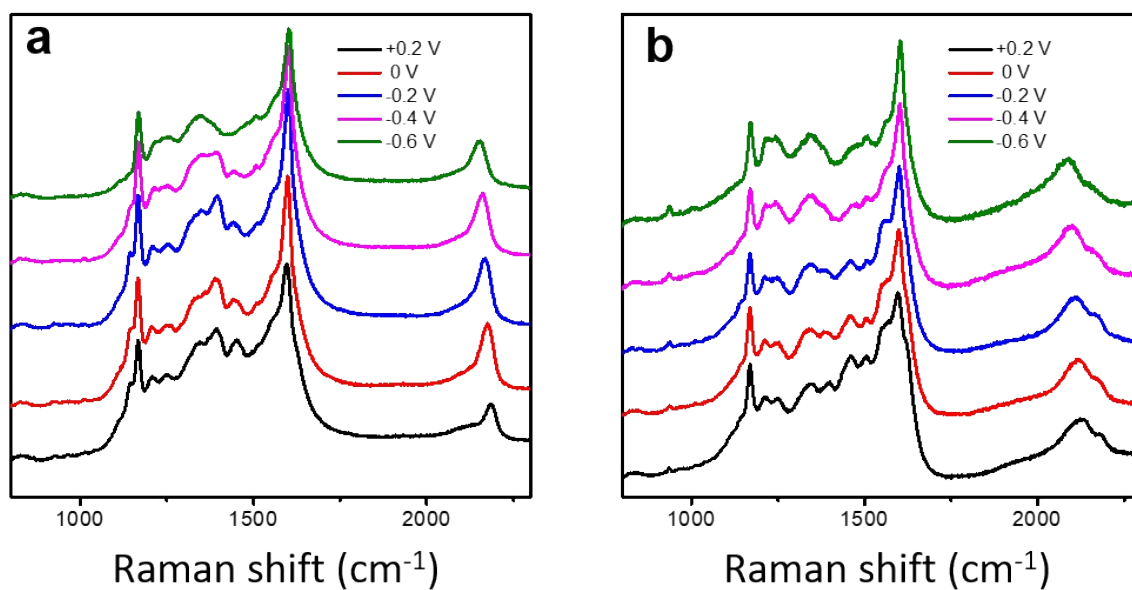


Figure S3. Potential-dependent full SERS spectra of (a) Ag nanoparticle on 1,4-PDI/Pt plate and (b) Pt nanoparticle on 1,4-PDI/Ag plate gap mode structures.

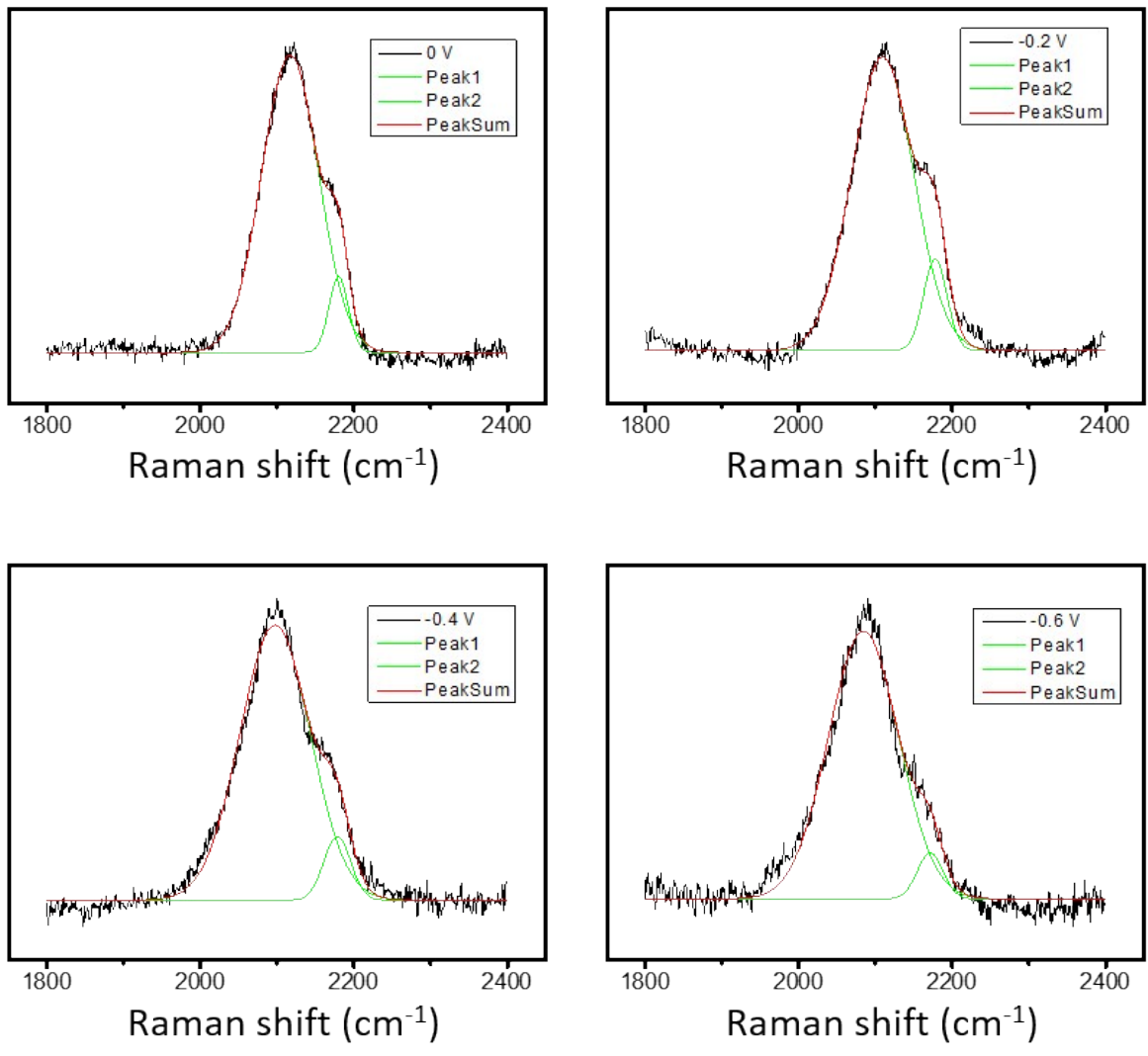
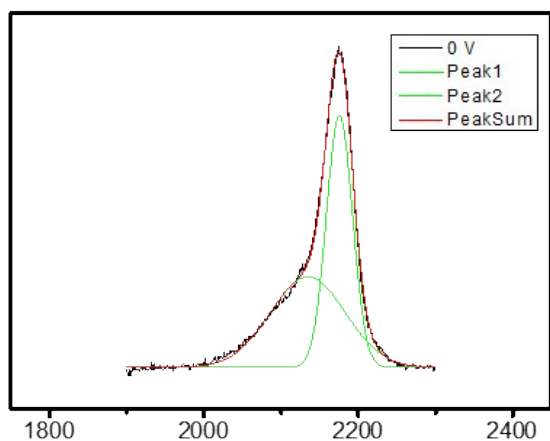
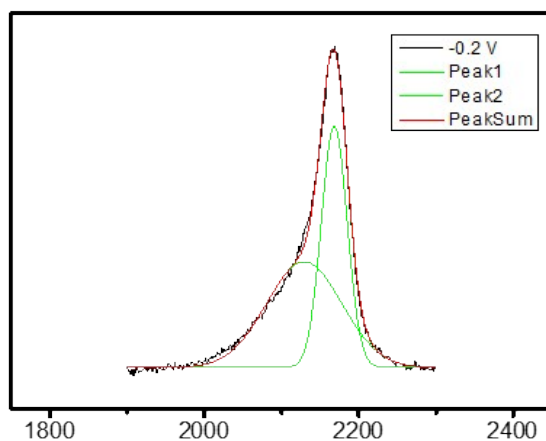


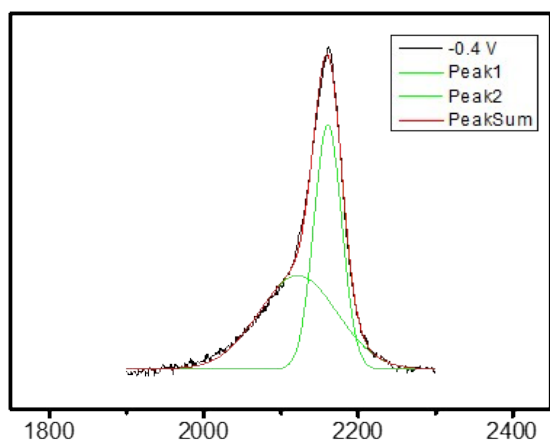
Figure S4. Deconvolution of NC stretching band from Pt nanoparticle on 1,4-PDI/Ag plate gap mode structure.



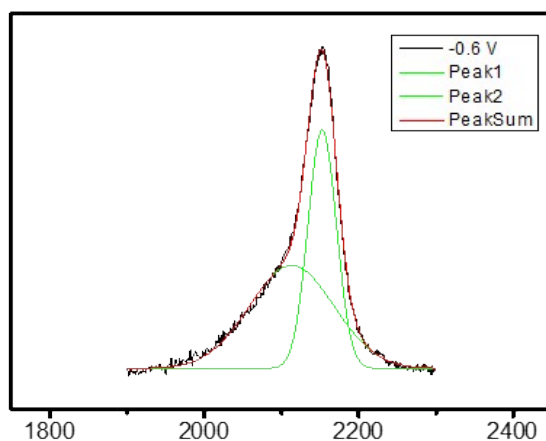
Raman shift (cm^{-1})



Raman shift (cm^{-1})



Raman shift (cm^{-1})



Raman shift (cm^{-1})

Figure S5. Deconvolution of NC stretching band from Ag nanoparticle on 1,4-PDI/Pt plate gap mode structure.

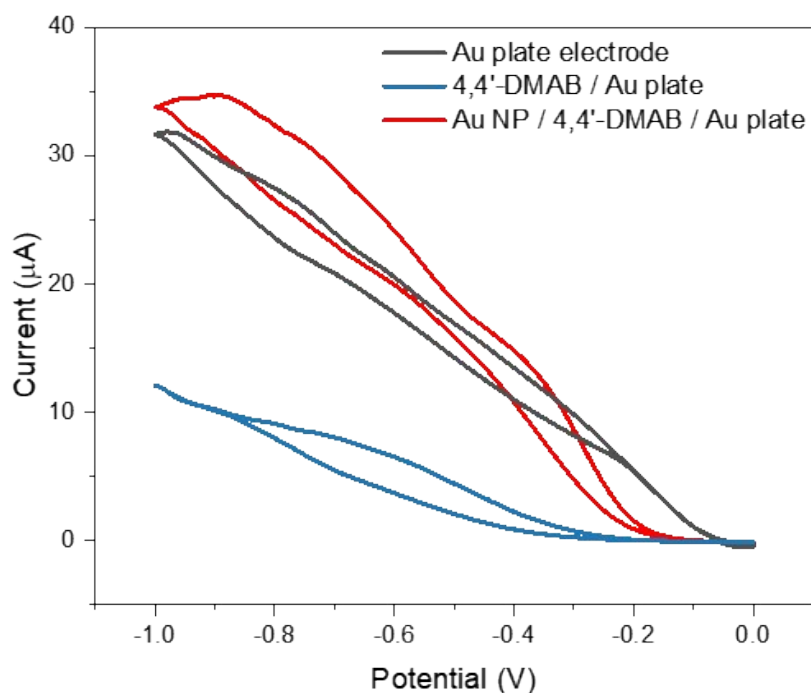


Figure S6. Cyclic voltammetry (CV) experiments show that the adsorbed nanoparticle at gap mode structure induces high electrical conductivity, compared to the 4,4'-DMAB coated Au plate. This implies that the charge transfer is fast at the molecular junction in gap mode structure so that the charges are temporally accumulated at the nanoparticle surface, inducing high effective potential than at the plate side. Such phenomena is presented by the more decreased NC peak position at the nanoparticle side in our heterogeneous gap mode structures.