Supporting Information

Tip-Enhanced Raman Imaging of Photocatalytic Reactions on Thermally-Reshaped Gold and Gold-Palladium Microplates

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Table S1: Probability of the appearance of N=N and DMAB on the center and edge of WAu@PdMPs.

Table S2: Catalyzed probability of Au, WAu, WAu@PdMPs

Experimental details

Chemical agents: 4-nitrobenzenethiol (4-NBT), polyvinylpyrrolidone (PVP, average molecular weight 40,000), diethylene glycol (DEG, 99%), gold (III) chloride trihydrate (HAuCl₄·3H₂O, 99.9%), hexadecyltrimethylammonium bromide (CTAB, 98%) and palladium (II) chloride were purchased from Sigma-Aldrich (St. Louis, MO). Ethanol was received from Decon Labs (King of Prussia, PA). H₂SO₄ (98%) and H₂O₂ (~30%) were purchased from Avantor (Center Valley, PA). No further purification was conducted for all chemicals. AFM tips were purchased from Appnano (Mountain View, CA); tips had 2.7 N/m force constant, 50-80 kHz resonance frequency.

Preparation of WAuMPs and WAu@PdMPs. The WAuMPs and WAu@PdMPs were prepared by thermal reshaping of AuMPs that has been previously described by Wang and Kurouski.¹ Briefly, AuMPs were prepared by adding the solutions of PVP (512 mg), CTAB (112 mg) and DEG (7.2 mL) into a flask. The mixture was heated in the sealed flask to 150 °C until surfactants were fully dissolved. Next, the solution of 9.6 mg HAuCl₄·3H₂O in 0.8 mL DEG was injected into the reaction flask; the temperature was kept constant at 150 °C for 5 min. After that, the flask was heated up to 200 °C and kept in this temperature for 45 min. The color change from yellow to transparent was observed; then slightly brown and finally golden color of the solution was detected. After cooled down to room temperature, reaction products were precipitated and centrifuged (8000 rpm, 3 min). Then the AuMPs were further purified by washing with ethanol and dissolving in ethanol to 50 ml for further use.

Au@PdMPs were prepared by a galvanic replacement reaction. First, 40 μ L of 20 mM ascorbic acid was added to 2ml of asprepared AuMPs stock solution following by stirring and addition of 40 μ L of 10 mM H₂PdCl₄. The reaction was kept at room temperature for 3 hours. Reaction products were purified by double centrifugation (5min at 5000 rcf) with removal of the supernatant. After that, the Au@PdMPs were re-dispersed in 2.0 mL of water and sonicated for 20 s.

For preparing of Walled microplates, a drop of solution that contained as-prepared WAuMPs or WAu@PdMPs was placed on a Si wafer and kept until drying at room temperature. Subsequently, the Si wafer with AuMPs or Au@PdMPs were rinsed with ethanol following by heating at 500 °C and kept for 2h at this temperature. Finally, the Si wafer was cooled down until reaching room temperature; the sample was sealed in a centrifuge tube prior to use for TERS imaging.

Modification of 4-NBT on AuMPs, WAuMPs, and WAu@PdMPs. As-prepared AuMPs, WAuMPs and WAu@PdMPs were first deposited on the pre-cleaned Si wafers. Then, a drop of 4-NBT (2mM) solution in ethanol was deposited on AuMPs (or WAuMPs and WAu@PdMPs). The sample was kept at room temperature for 2 h allowing for the formation thiol-gold bond between 4-NBT and Au and a monolayer of 4-NBT molecule on the surface of microplates. Finally, the sample was rinsed with ethanol for three times and sonicated for the removal of free 4-NBT.

TERS Probe Fabrication. Appnano AFM tips were mounted onto the surface of glass coverslips and placed in the thermal evaporator (MBrown, Stratham, NH). Metal evaporatoin was carried out at $\sim 1 \times 10^{-6}$ mbar by the evaporation of gold pellets (Kurt

J. Lesker, Efferson Hills, PA) with 0.1 A/s rate. Finally, a layer of 70 nm of Au was deposited on each of the AFM tip. The tip surface was ~50 °C during metal deposition.

AFM-TER Imaging. AFM and TER images were collected on AIST-NT-HORIBA system equipped by 633 nm continuous wavelength (CW) laser. Laser light was brought to the sample in a side-illumination geometry using 100× Mitutoyo microscope objective. Scattered electromagnetic radiation was collected using the same objective and directed into HORIBA iHR550 spectrograph equipped with a Synapse EM-CCD camera (HORIBA, Edison, NJ). The laser power was 30 µw for all the TERS experiment in this work and the acquisition time was 0.5 s per spectrum. The signal intensities of the nitro, azo group, and amino group in all of our TERS images are integrated intensities of 1300-1370 cm⁻¹, 1380-1460 cm⁻¹ and 1480-1520 cm⁻¹, 1580-1600 cm⁻¹ respectively.

DFT calculations. All calculations were performed using a development version of NWChem.² Unconstrained geometry optimization was performed using the PBE exchange-correlation functional³ in conjunction with the def2-TZVP basis⁴ set and a fitting basis⁵ for the evaluation of the Coulomb potential. Ensemble-averaged Raman spectra and vibrational mode-dependent molecular polarizability derivatives were computed using the CPKS method, as implemented in NWChem.² Ensemble-averaged Raman scattering activities (*Sm*) are given by^{6,7}

$$S_m = g_m [45\alpha_m^{+2} + 7\beta_m^{+2}] \tag{1}$$

where

$$\alpha'_{m} = \frac{1}{3} (\tilde{\alpha}_{xx,m} + \tilde{\alpha}_{yy,m} + \tilde{\alpha}_{zz,m})$$
(2)

and

$$\beta_{m}^{'2} = \frac{1}{2} \left[\left(\tilde{\alpha}_{xx,m} - \tilde{\alpha}_{yy,m} \right)^{2} + \left(\tilde{\alpha}_{yy,m} - \tilde{\alpha}_{zz,m} \right)^{2} + \left(\tilde{\alpha}_{zz,m} - \tilde{\alpha}_{xx,m} \right)^{2} + 6 \left(\tilde{\alpha}_{xy,m}^{'2} + \tilde{\alpha}_{xz,m}^{'2} + \tilde{\alpha}_{yz,m}^{'2} \right) \right]$$
(3)

In the above equations, g_m is the vibrational state degeneracy and primes denote derivatives with respect to the m^{th} state, α'_m/β'_m^2 are the isotropic/anisotropic polarizabilies, and $\tilde{\alpha}_{ij,m}(i,j=x,y,z)$ are components of the polarizability tensor.

The spectrum of an oriented molecule can be simulated according to^x

$$S_n^2 \alpha \sum_n \left| \vec{E}_s^L R_z^T R_y^T R_x^T \tilde{\alpha}_n^T R_z R_y R_x \vec{E}_i^L \right|^2 \tag{4}$$

Here, molecular polarizability derivative tensor elements (a_n) of a molecule are oriented with respect to the vector components of the local electric fields along incidence and scattering directions in the TER geometry $(\vec{E}_{i,s}^L = \vec{E}_z^L)$ after (i) projection

of the molecular onto the laboratory frame, and (ii) rotating the molecule (using rotation matrices $R_{x,y,z}$ and $R_{x,y,z}^{T}$). We will revisit this analysis in the ensuing sections of this work.



Scheme S1. Illustration for the preparation of (a) WAuMPs and (b) WAu@PdMPs.



Fig. S1. (a) FE-SEM image of WAu@PdMPs. (b) FE-SEM LABE (Low angle backscattered electron image) micrograph of WAu@PdMPs. (c) EDS analysis of Au@PdMPs.



Fig. S2 (a) AFM image of WAu@PdMP. (b) Height profile of WAu@PdMP.



Fig. S3. (a)- (c) AFM (bottom) images of WAu@Pd MPs. (d)- (f) Overlapping TERS image of NO₂ vibration and DMAB vibration on WAu@PdMPs. Intensity of 1339 cm⁻¹ band (NO₂ vibration) of 4-NBT is shown in blue, intensities of 1397 and 1451 cm⁻¹ (N=N vibration) of DMAB is shown in red. (g)- (i) Overlapping TERS image of NO₂ vibration and NH₂ vibration on WAu@PdMPs. Intensity of 1339 cm⁻¹ band (NO₂ vibration) of 4-NBT is shown in blue, intensities of 1485,1586 cm⁻¹ (NH₂ vibration) is shown in green. (j)- (l) Typical TERS spectra extracted from chemical maps on WAu@PdMPs showing presence of 4-NBT (blue), DMAB (red) and 4-ATP (green). The resolution in each of TERS image is 20 nm per pixel.



Fig. S4 Probability of the appearance of N=N and DMAB on the center and edge/corners of WAu@PdMPs.



Fig. S5. (a) TERS image of 4-ATP (band 1485 cm⁻¹) on WAuMPs (20 nm per pixel). (b) Overlapping TERS image of NO₂ vibration with 4-ATP vibration on WAuMPs. Intensity of 1339 cm⁻¹ band (NO₂ vibration) of 4-NBT is shown in blue, intensities of 1485 cm⁻¹ (NH₂ vibration) is shown in green. (c) In-situ AFM images of WAuMPs during TERS imaging. (d) Randomly picked up TERS spectra collected on WAuMPs, corresponding numbers have been marked in (b). No NH₂ band at 1485 cm⁻¹ can observed on WAuMPs.



Fig. S6. (a) AFM images of AuMPs and (e) WAuMPs. TERS images of (b, c, d) AuMPs and (f, g, h) WAuMPs (20 nm per pixel). Intensity of 1339 cm⁻¹ band (NO₂) of 4-NBT is shown in blue, intensities of 1397 and 1441 cm⁻¹ (azo) of DMAB is shown in red. (i-l) Typical TERS spectra extracted from chemical maps on (b and f) showing presence of 4-NBT (blue). Typical TERS spectra randomly picked up from chemical maps on (c and g) showing presence of DMAB (red).









Fig. S8. (a)- (d) High resolution overlapping TERS image of NO₂ vibration and N=N vibration on WAu@PdMPs. Intensity of 1339 cm⁻¹ band (NO₂ vibration) of 4-NBT is shown in blue, intensities of 1397 and 1447 cm⁻¹ (N=N vibration) of DMAB is shown in red. (e)- (h) High resolution overlapping TERS image of NO₂ vibration and NH₂ vibration on WAu@PdMPs. Intensity of 1339 cm⁻¹ band (NO₂ vibration) of 4-NBT is shown in blue, intensities of 1485,1586 cm⁻¹ (NH₂ vibration) is shown in green. (i)- (l) Corresponding AFM images of TERS mapping on WAu@PdMPs. (m)- (o) Typical TERS spectra extracted from high resolution chemical maps on WAu@PdMPs showing presence of 4-NBT (blue), DMAB (red) and 4-ATP (green). The resolution in TERS image (Figure a, b, e and f) is 5 nm per pixel, 4 nm for Figure c and g, 3.5 nm for Figure d and h.



Fig. S9. DFT calculations of cis-DMAB.



Fig. S10. (a) TERS image of 4-ATP (band 1485 cm⁻¹) on AuMPs (20 nm per pixel). (b) Overlapping TERS image of NO₂ vibration with 4-ATP vibration on AuMPs. Intensity of 1339 cm⁻¹ band (NO₂ vibration) of 4-NBT is shown in blue, intensities of 1485 cm⁻¹ (NH₂ vibration) is shown in green. (c) In-situ AFM images of AuMPs during TERS imaging. (d) Randomly picked up TERS spectra collected on AuMPs, corresponding numbers have been marked in (b). No NH₂ band at 1485 cm⁻¹ can observed on AuMPs.

Table S1: Probability of the appearance of N=N and DMAB on the center and edge/corners of WAu@PdMPs.

	Center	Edge/corners
N=N	(2334/4913) 47.5 %	(954/2112) 45.2 %
NH_2	(836/4913) 17.0 %	(394/2112) 18.6 %

Table S2: Yield of reaction products on hot carrier driven reduction of 4-NBT on AuMPs, WAuMPs and WAu@PdMPs.

	NO₂ Counts	N=N Counts (percents)	NH₂ Counts (percents)
AuMPs	3898	2853 (73.2%)	0
WAuMPs	3270	146 (4.46%)	0
WAu@PdMPs	7025	3288 (46.8%)	1230 (17.5%)

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