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Supplementary Materials for

The Golden Gate to Photocatalytic Hydrogen Production

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1 PHOTOCATALYST SYNTHESIS

1.1 Synthesis of Cadmium Selenide Quantum Dots (CdSe QDs)[1,2]:

For the synthesis of CdSe QDs, 60mg cadmium oxide (CdO), 3g trioctylphosphine oxide (TOPO), and 280mg octadecylphosponic acid (ODPA) were mixed in a three neck flask. The mixture was put under argon and heated to 150 °C. At this point the solution was put under vacuum for 30min and then returned to Ar. The solution was heated to 370 °C, at which point trioctylphosphine (TOP) was added to the clear solution. After the temperature recovered to the previous point a solution of TOP, and selenium was injected into the flask. After a set amount of time (0-5min depending on the desired size), the solution was removed from heat. Once cool, toluene was added to the solution which was cleaned by repeated precipitation by methanol and redissolution in toluene. The resultant solution was characterized by absorption spectroscopy for use in the growth of CdSe@CdS.

1.2 Synthesis of Cadmium Sulfide Seeded Rods (CdSe@CdS)[2,3]:

For the synthesis of CdSe@CdS, CdO, TOPO, hexylphosphonic acid (HPA), and ODPA were mixed in a three neck flask (see table S1 for examples). The mixture was put under argon. After various heating/vacuum stages (depending on the method) a final temperature was reached (320-380 °C, also depending on the method), at which point 1.5g TOP was added to the clear solution. After the temperature recovered to the previous point a mixture of 1.5g TOP, 120mg sulfur, and CdSe QDs were injected into the flask, and were left for eight or more minutes. The CdSe used for injection was collected by drying a desired volume of seeds, which were then redissolved in TOP. After a desired amount of time the solution was removed from heat. Once cool, toluene was added to the solution. The rods were cleaned by repeated redissolution in combinations of toluene, hexane, octylamine and nonanoic acid, and precipitated by centrifugation with methanol as the non-solvent. A final cleaning step was done in order remove short rods, seeds and tetrapods, using toluene, isopropanol and a centrifugation at 4000 rpm for 30 minutes. Finally, the pellet was redissolved in toluene. Successful synthesis and cleaning resulted in uniform rods of high quality and quantity (Figure S1) which were used for further experimentation.

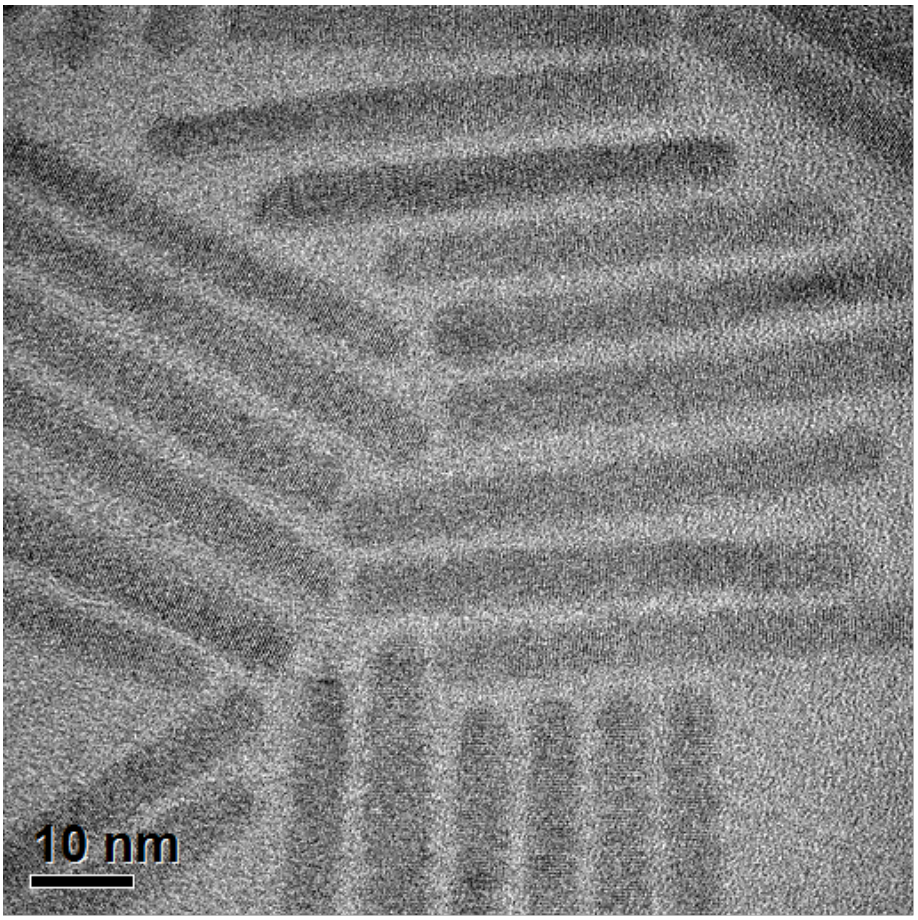

Figure S1. Typical TEM micrograph of as grown CdSe@CdS nanoparticles

Resultant CdSe@CdS Rod Length	32.7 ± 3.6	44.7 ± 3.1	50.4 ± 4.1
TOPO (g)	3.3	3	3
ODPA (g)	1.08	0.29	0.29
HPA (mg)	80	80	80
CdO (mg)	207	60	60
Seeds (uL) [diameter in nm][3,4]	400 [3.0]	350 [2.5]	350 [2.5]
Reaction Temp (°C)	320	360	380
Reaction Time	10 min	8 min	15 min

Table S1. Typical precursor amounts and conditions for CdSe@CdS growth

2 METAL COCATALYST DEPOSITION

2.1 Growth of Gold Metal Tips on CdSe@CdS Nanorods (Au-NR):

Growth of Au-NR was loosely based on previous photodeposition of gold on CdS and CdSe@CdS.[5] A solution of gold chloride ($AuCl_3$, 2mg/mL) and didodecyldimethylammoniumbromide (DDAB, 12mg/mL) in toluene was prepared inside a glovebox under an inert atmosphere. 600µL of this solution was mixed in a cuvette with 1.5mL of CdSe@CdS in toluene, which was prepared as described above. Still inside the glovebox, the cuvette was placed in a holder (Thorlabs Cuvette Holder – CVH100) and illuminated while stirring by a 455nm LED at 200mW of power (Thorlabs Mounted High Power LED – M455L3). After 2 hours of illumination the sample was collected in a centrifuge tube and precipitated by centrifugation using methanol as a non-solvent. The dark-red pellet was redissolved in toluene for further study and experimentation. Analysis of photoluminescence of capped rods versus uncapped rods was used for a rough estimation of the percent capped rods, as the metal tips quench photoluminescent reemission.[6]

2.2 Growth of Platinum Metal Tips on CdSe@CdS Nanorods (Pt-NR):

Growth of Pt-NR was loosely based on previously reported photodeposition of platinum on CdS and CdSe@CdS.[7] For the growth of Pt-NR, dimethylplatinum cyclooctadiene (Me_2PtCOD, 20mM) in toluene was prepared inside a glovebox under an inert atmosphere. 1.8mL of this solution was mixed in a cuvette with 200µL triethylamine (TEA) and 1.5mL of CdSe@CdS in toluene. The mixture was processed exactly like Au-NR rods, except the LED illumination was continued for 8 hours. In the case of **Au@Pt-NR** growth, the procedure for Pt-NR growth was carried out except Au-NR were used in place of bare CdSe@CdS.

2.3 Growth of Gold-Platinum Bimetal Tips on CdSe@CdS Nanorods (AuPt-NR):

For the growth of AuPt-NR, solutions of Me_2PtCOD, and $AuCl_3$/DDAB were prepared as above. 1.5mL of CdSe@CdS rods was mixed with 1.1mL of the Me_2PtCOD solution, 500µL of the AuCl3/DDAB solution, and 200µL of TEA. These solutions were mixed in a cuvette and were processed exactly like Au-NR and Pt-NR rods, except the LED illumination was continued for 6 hours.

2.4 Characterization of Particles:

UV-Vis absorption spectroscopy was done using an Agilent Cary 5000 UV-Vis-NIR spectrophotometer using standard 10mm fluorometer cuvettes. Spectra were studied using the accompanying Cary WinUV software package. Spectra were used frequently to determine seed size, seed concentration, rod concentration, and the absorbance (Abs) of solutions used for hydrogen production.

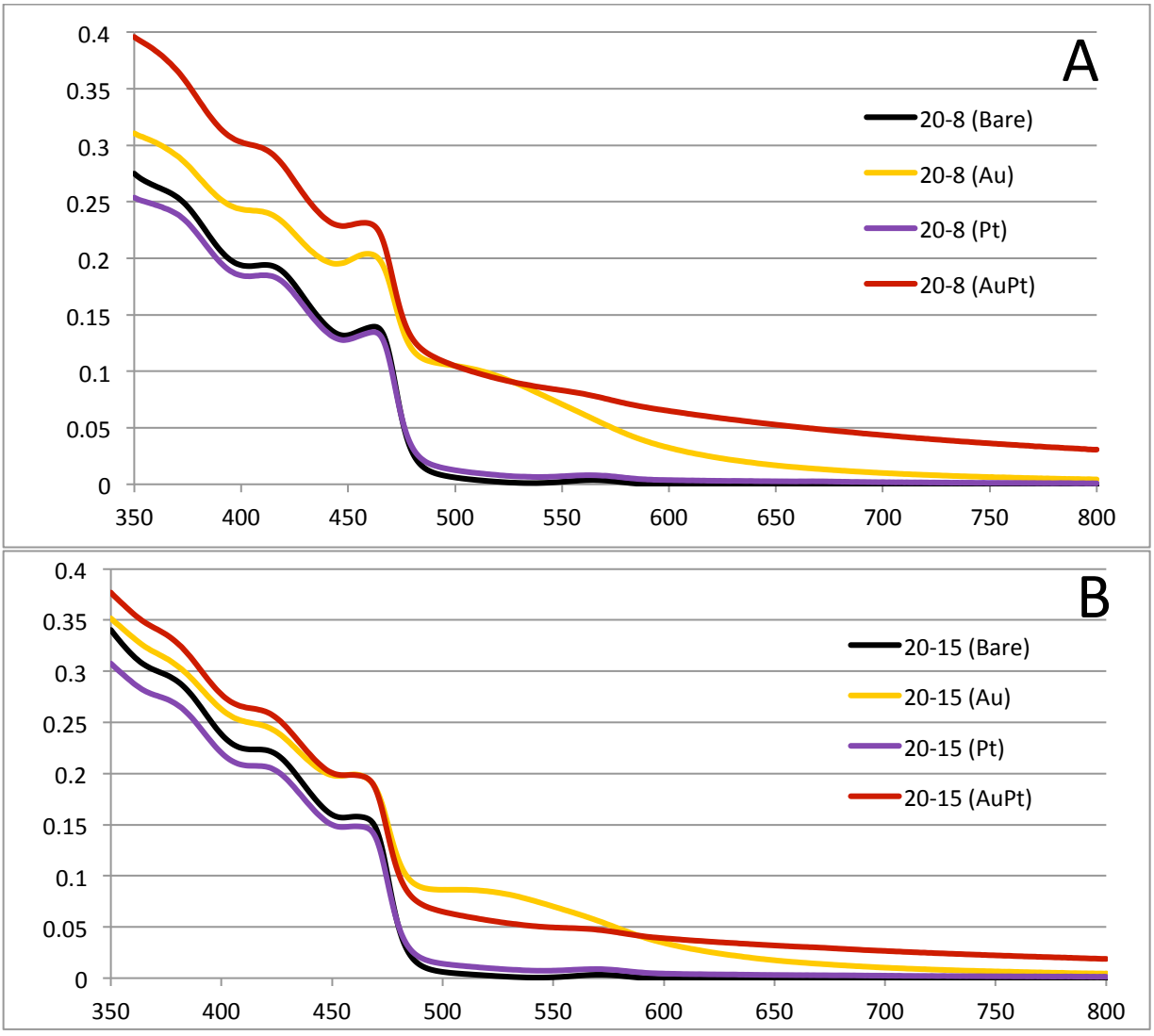

Figure S2: UV-Vis spectra for (A) 45nm rods with 2.51nm seed (B) 40nm rods with 2.51nm seed. Each series show the spectra for bare rods (black), Au capped rods (orange), Pt capped rods (purple), and AuPt bimetal capped rods (red).

3 Hydrogen Production Measurement

3.1 Ligand Exchange:

CdSe@CdS, Au-NR, Pt-NR, Au@Pt-NR and AuPt-NR were transferred from toluene to water using established protocols.[8] Briefly, ligand exchange was performed by precipitating the rods, using centrifugation with methanol as the non-solvent. The pellet was then redissolved in a mixture of methanol, mercaptoundecanoic acid (MUA), and tetramethylammonium hydroxide (TMAH). Once dissolved the rods were precipitated out using toluene as a non-solvent and further centrifugation. This pellet was then dissolved in water, methanol, or other polar solvent as desired.

3.2 Determining the Hydrogen Production Rate:

Rods solutions were moved to ultrapure water by MUA ligand exchange, this first step was done as soon as possible before starting a new measurement, and usually less than one hour before the cell was first purged. Solutions were diluted using ultrapure water to 9.9mL, and then 1.1mL of isopropanol (IPA) was added to give a 10% solution. For most experiments, and for all comparative series, the entire photodeposition product (prepared by the methods above) was used, so that the number of rods in solution was consistent between different measurements. When bare rods were measured, 1.5mL of CdSe@CdS stock solution was similarly used to maintain the same concentration. Due to the differences in concentration of CdSe@CdS sources, comparisons of series using the same rods source can be confidently compared, while samples using different rod sources may differ based on the nanorods or the nanorod concentration.

The 11mL solution was placed in a reaction cell (Figure S3), and 100µL was removed before the cell was sealed. This 100µL was diluted ten-fold, and used for UV-Vis measurements of the true solution, and sometimes saved for TEM imaging of the solution from before illumination. The reaction cell was closed and connected to a 10mL/min argon line (inlet) and an Agilent 7890A gas chromatograph with a thermal conductivity detector (GC-TCD) (outlet). Gas was continually flowed through the cell in the dark while the solution was stirred and gas samples were automatically taken every 5 minutes for measurement. Once the hydrogen, oxygen and nitrogen

gas signals (from air) were below the detection limit, the light source was turned on and the cell was illuminated through a quartz window.

Once illuminated, a hydrogen peak was observed, and the integrated area of this peak was used for photocatalytic quantum efficiency (QE%) calculations. Each hydrogen molecule production requires two electrons, and therefore two photons. Thus the apparent quantum efficiency of the sample is defined as QE $= 2N_{H_2}/N_{h\upsilon}$.

The number of photons was calculated by using the measured LED power (which was adjusted to a desired value and measured using a Thorlabs Digital Optical Meter – PM206) assuming that all photons had a wavelength of 455nm ($4.366*10^{-19}$ Joule/photon). A common LED power of 100mW (0.1 Joule/sec), produced 2.2910^{17} photons/sec. The number of hydrogen molecules produced was determined based on the area of the hydrogen gas peak, from the TCD. The GC was calibrated using a calibration cell that is identical to the reaction cell, except that it has two nickel electrodes for electrolysis. A plot of current (electrons/second) vs. peak area gave a linear relationship whose slope was used to convert the GC-TCD signal into the number of hydrogen molecules generated.

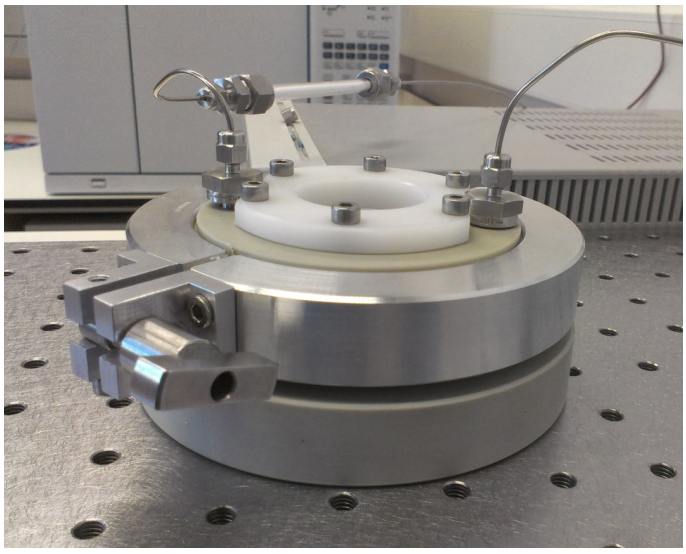

Figure S3. Photograph of the gas-tight reaction cell with GC seen in the background.

3.3 Sample Stability

All samples demonstrated reasonable stability over time, as can be seen in Figure S4, which presents a time line for hydrogen production efficiencies. Moderate decrease in activity with time is likely caused by consumption and evaporation of the hole scavenger (IPA).

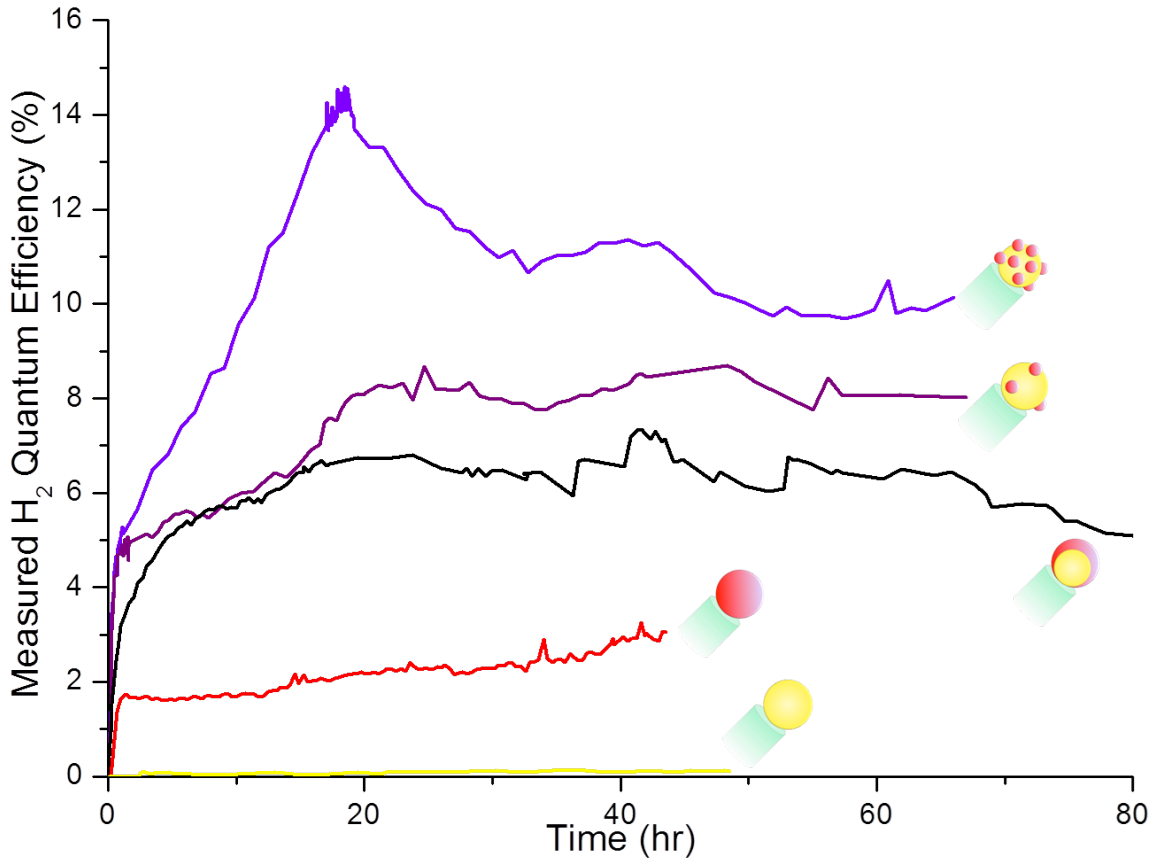

Figure S4. Samples stability. Measurement of H_2 production quantum efficency over time utilizing CdSe@CdS nanorods decorated with different metal cocatalysts serving as the reduction site: Au (yellow), Pt (red), Au@Pt core shell and Au-Pt islands.

4 STRUCTURAL CHARACTERIZATION

Transmission Electron Microscopy (TEM) was done on a FEI Tecnai G^2 T20 S-Twin TEM, running at 200 kV with a LaB_6 electron source, and on a FEI image aberration-corrected Titan 80-300 FEG S/TEM operated at 300 keV. The FEI Titan was also used for High Angle Annular Dark Field Scanning Transmission Electron Microscopy (HAADF-STEM). Samples for TEM were prepared by either dropping the solution directly or by aerosolized spray onto 300 mesh ultrathin carbon on lacey carbon grids purchased from Ted Pella Inc.

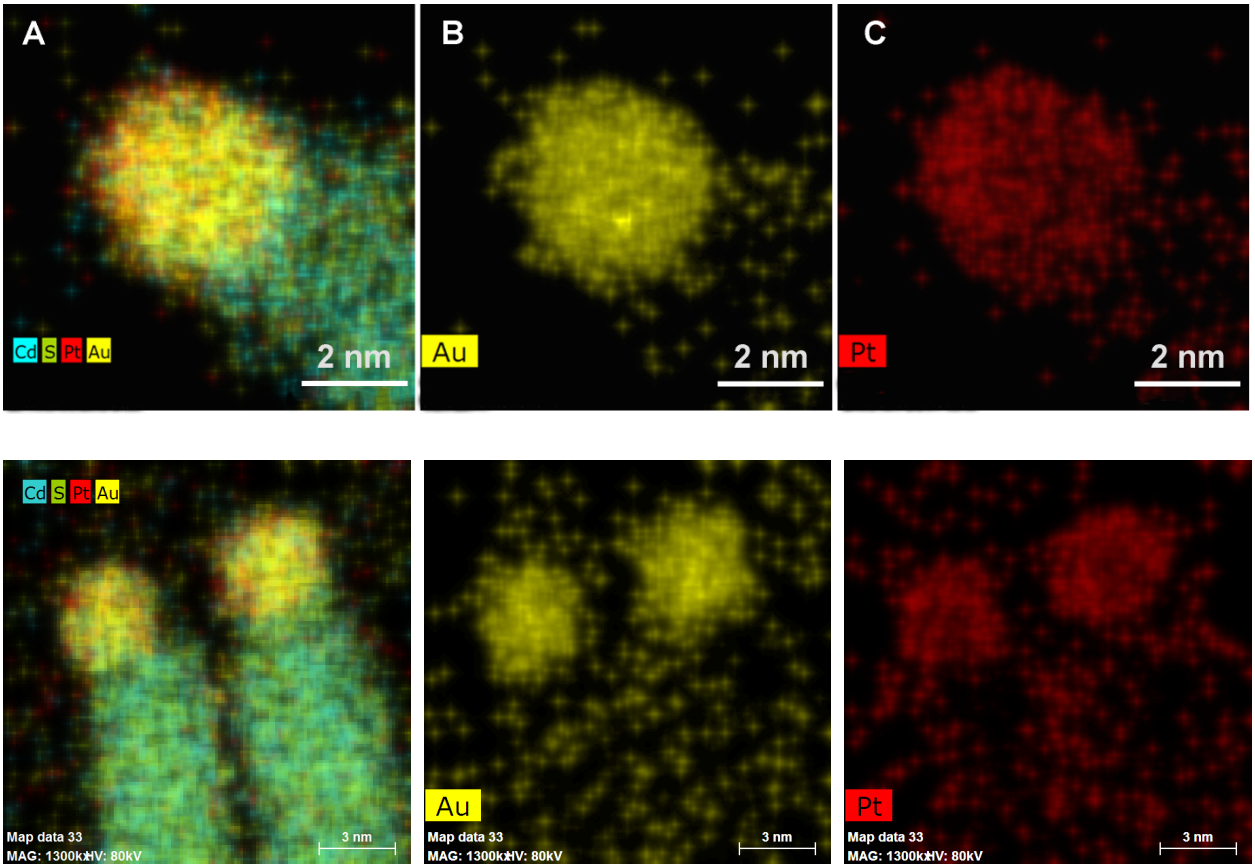

Figure S5. EDS elemental maps of the bimetallic tip, demonstrating the formation of a Au core that is decorated with islands of Pt.

Atomic-resolution STEM images and EDS maps were recorded at an accelerating voltage of 80 kV in a probe aberration-corrected FEI Titan G2 60-200 ChemiSTEM microscope equipped with a high-brightness FEG. HAADF images were recorded with a Fischione Model 3000 detector with a semi-convergence angle of 23.8 mrad, a probe current of 40 pA, and an inner collection

angle of 99.0 mrad. EDS spectrum image data were obtained with a Bruker Super-X four-segment SDD detector with a probe semi-convergence angle of 35.9 mrad, a beam current of 290 pA and a total recording time between 180 s and 600 s. Quantitative maps were calculated with the Bruker Esprit software, through background subtraction, spectrum deconvolution. Additional EDS elemental maps (non-background subtracted) are presented in figure S5.

5 SI REFERENCES

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