

Supporting Information

Plasmonic Support-Mediated Activation of 1 nm Platinum Clusters

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1. Extinction spectra and AFM image of bare gold films of different thickness

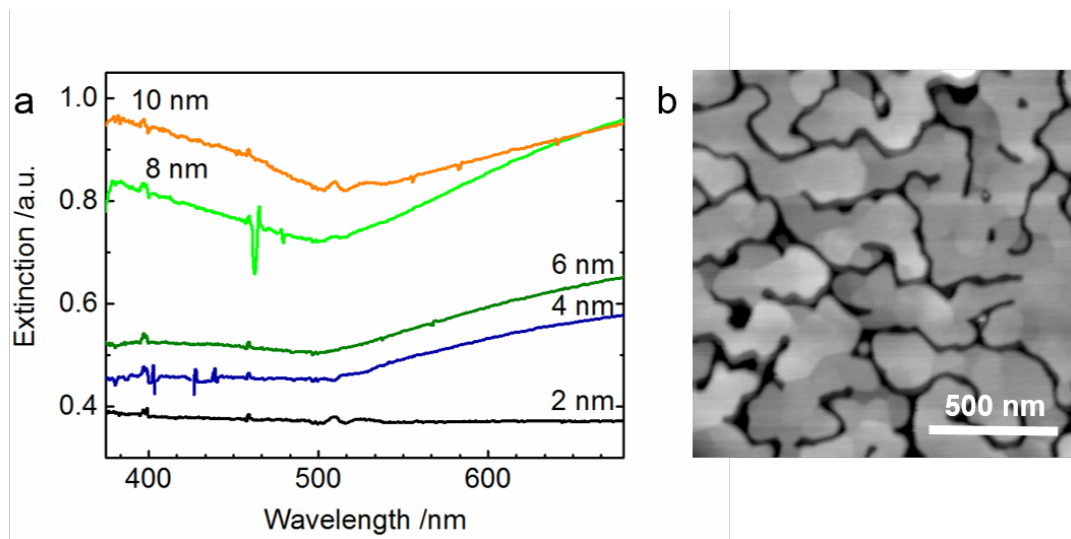


Figure S1 (a) UV-VIS spectra of gold films of different thickness supported on a 5 nm Pt film/sapphire. The background extinction is due to the reflectivity of the substrate-film interface. (b) AFM image of a 10 nm Au film sample showing the morphology of large, flat and interconnected islands. XPS shows no contamination of the Au surface by Pt.¹

2. Absorption of bare gold films after annealing to 120° C

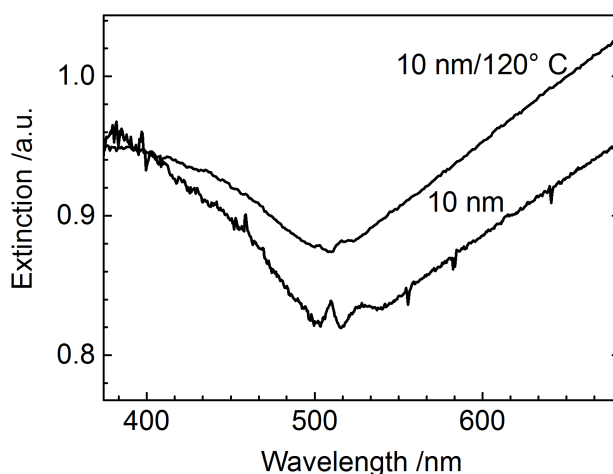


Figure S2 UV-VIS spectra of a 10 nm Au film, supported on a 5 nm Pt film/sapphire, before and after annealing to 120° C in UHV, the degassing temperature used for our samples before the STM measurements.

3. HAADF-STEM micrograph and statistical evaluation

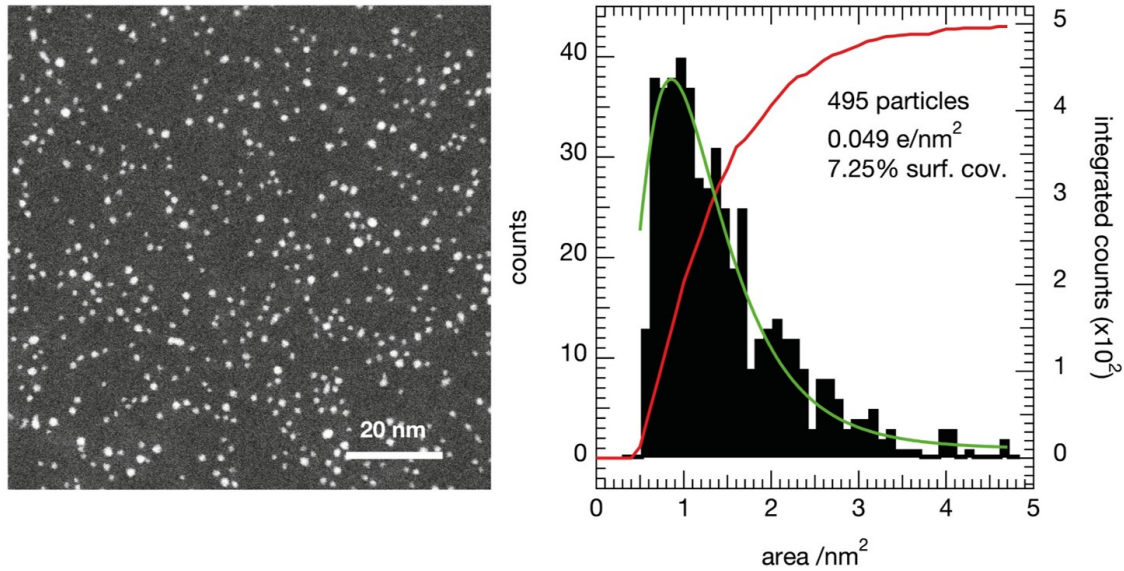


Figure S3 Representative high-angle annular dark field - scanning transmission electron microscope (HAADF-STEM) micrograph of Pt_{n>35} clusters that highlights the relatively homogenous size distribution of intact clusters (46±10 atoms) achieved by mass high-pass filtering and soft landing conditions,^{2, 3} as well as low (7.25%) surface coverage. The right plot shows the area distribution function along with a log-normal fit, typical for unselected cluster samples.⁴

4. Absorption of gold film-supported Pt clusters

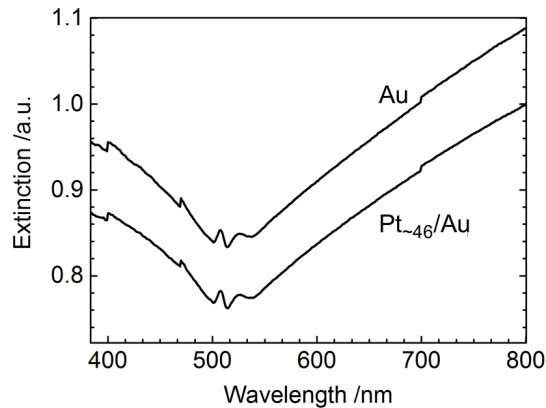


Figure S4 UV-VIS spectra of Pt clusters supported on the 10 nm thick gold film. Spectra are offset for clarity.

5. Calculation of the quantum efficiency

Based on the catalytic MB decomposition activity measurements for the submonolayer coverage of 7% Pt on the thin gold film, a quantum yield can be estimated. We calculate an external quantum efficiency (EQE) of $\sim 0.0006\%$ and an internal quantum efficiency (IQE) of $\sim 0.002\%$. Assumptions: 1 photon is needed to decompose 1 MB molecule; 30% of the plasmons decay to hot carriers.; 100% of hot electrons are transferred into MB.⁵

Note that the dry MB film does not allow dye molecules to diffuse.

6. Extinction spectra and calibration line of methylene blue (MB) in ethanol

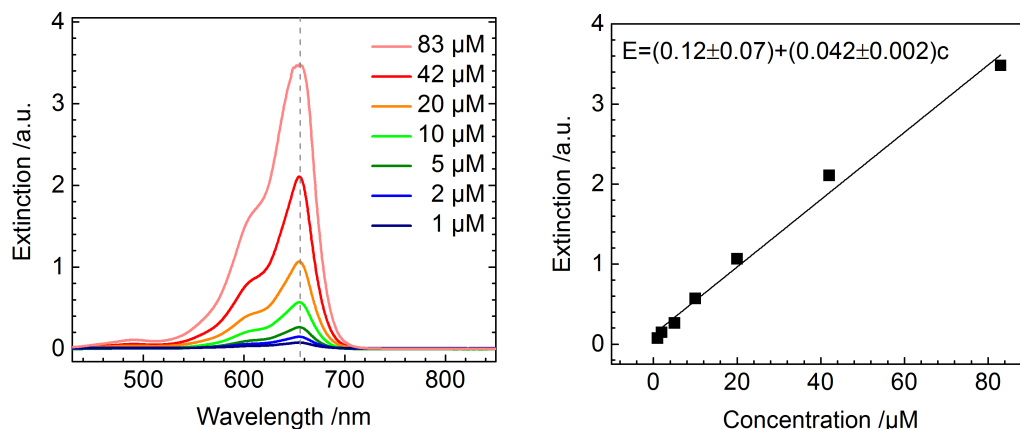


Figure S5 Left: UV-VIS spectra of different concentrations of MB in ethanol, showing a maximum at 657 nm (dashed line). Right: Calibration line for MB with indication of the fit parameters, based on the extinction value taken at 657 nm (left graph).

7. The effect of illumination on the appearance of the gold film in STM

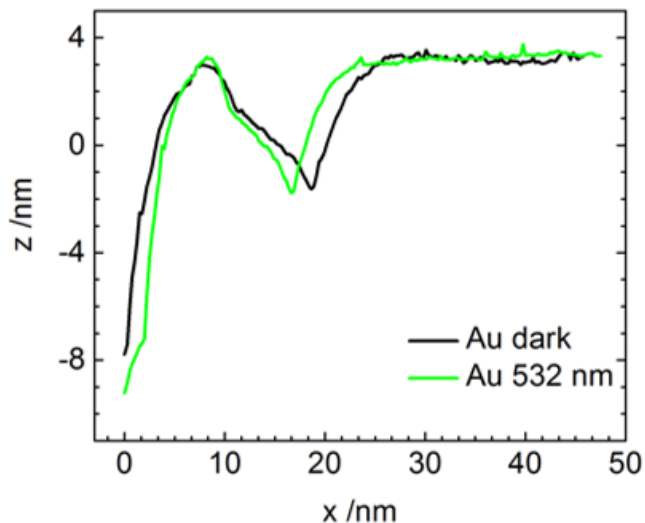


Figure S6 Step edge profiles of the Au film support with (green) and without (black) laser illumination. Tunneling parameters: $I_t = 5$ pA, $V_t = 1$ V. No significant changes in the apparent step height are observed, indicating that the surface plasmon excitation of the gold film has the same electronic effect along the whole surface and in particular along steps. This is in contrast to the observation for Pt-Au junctions, at Pt nanoclusters, where the apparent cluster height decreases upon illumination.

Additional SI References

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