

Supplementary Information

Decoding the kinetic limitations of plasmon catalysis: the case of 4-nitrothiophenol dimerization

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1. Calculation of Absorption Time

We assumed that the geometrical cross-section of the particles is about the same as their absorption cross-section¹. In this case the photon arrival frequency f_{photon} is:

$$f_{\text{photons}} = I \cdot \pi r^2 \cdot \frac{\lambda}{hc} = 2 \text{ THz} \quad (\text{S1})$$

with $I = 25 \text{ kW/cm}^2$, $r = 25 \text{ nm}$, $\lambda_{\text{Laser}} = 785 \text{ nm}$. For the time between the arrival of two photons this gives $T_{\text{photon}} = 1/f_{\text{photons}} = 0.5 \text{ ps}$, which is sufficient to trigger the reaction.

2. Low Intensity SERS

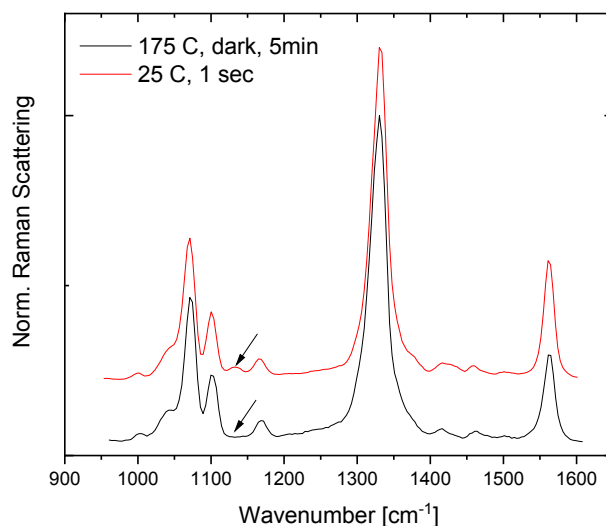


Figure S1. Comparison between Raman spectra taken after 5min reaction time at 175°C ambient temperature under dark conditions (black line) and 1 sec reaction time at 25°C with an illumination of 25 kW/cm². The latter intensity causes a photoheating by 18 K to 43°C. Increasing the ambient temperature above 180°C led to melting of the particles.

3. Reaction Kinetics

3.1 Product Peak P_1

The dimerization of two reactant molecules R to one product molecule P , is a bimolecular reaction according to the scheme²:



The kinetics of the reaction can be obtained from the corresponding differential equation:

$$-2 \frac{d[P]}{dt} = \frac{d[R]}{dt} = -k_2[R]^2 \quad (S3)$$

Were $[R]$ and $[P]$ are the concentrations of reactant and product and k_2 is the second order rate constant. This DGL must be integrated with respect to time to obtain an expression for reactant a given point in time $[R(t)]$:

$$\int_{R_0}^{R_t} \frac{d[R]}{[R]^2} = \int_0^t -k_2 dt \Rightarrow -\frac{1}{[R]} \Big|_{R_0}^{R_t} = -kt \Leftrightarrow \frac{1}{[R]_0} - \frac{1}{[R]_t} = k_2 t \quad (\text{S4})$$

This simplifies to:

$$[R]_t = \frac{1}{k_2 t + 1/[R]_0} = \frac{[R]_0}{1 + [R]_0 \cdot k_2 t} \quad (\text{S5})$$

The product concentration $[P(t)]$ at a given time t is then obtained by:

$$[P(t)] = \frac{[R]_0 - [R]_t}{2} = \frac{[R]_0}{2} \left(1 - \frac{1}{1 + [R]_0 k_2 t} \right) = \frac{[R]_0}{2} \cdot \frac{([R]_0 k_2 t)}{1 + [R]_0 k_2 t} = \frac{1}{2} \cdot \frac{[R]_0^2 k_2 t}{1 + [R]_0 k_2 t} \quad (\text{S6})$$

To obtain the Raman signal of the P_1 product peak of DMAB, we must multiply this concentration by the Raman cross-section of the peak σ_{P_1} . For simplicity, the cross-section shall also include the SERS enhancement factor. This approach is legitimate, as we expect that the enhancement does not change during the course of the reaction. For the Raman intensity of the peak P_1 we thus get:

$$I_{P_1}(t) = \sigma_{P_1} \frac{1}{2} \cdot \frac{[R]_0^2 k_2 t}{1 + [R]_0 k_2 t} + I_0 \quad (\text{S7})$$

Here I_0 is an additional fitting component, that takes into account a small non-zero background at the start of the reaction.

3.2 Reactant Peak R_2

The fraction of the reactant peak R_2 that decays because of the production of DMAB can be easily obtained by multiplying equation S5 with the Raman cross-section of the R_2 peak σ_{R_2} . However, we assume that 4NTP does not only react to DMAB, but also has a parallel first order

reaction route, which we must include to obtain an expression for the intensity $I_{R_1}(t)$. The corresponding differential equation is:

$$\frac{d[R]}{dt} = -k_1[R] \quad (\text{S8})$$

With the solution:

$$[R] = [R]_0 \cdot e^{-k_1 t} \quad (\text{S9})$$

The progression of the peak R_2 during the reaction is hence given by:

$$\begin{aligned} I_R(t) &= \sigma_{R_2} \frac{[R]_{0,dim}}{1 + [R]_{0,dim} \cdot k_2 t} \\ &+ \sigma_{R_2} [R]_{0,diss} \cdot e^{-k_1 t} \\ &+ \sigma_{R_2} [R]_{0,inert} \end{aligned} \quad (\text{S10})$$

Here $[R]_{0,cat}$ is the fraction of 4NTP that dimerizes to DMAB, $[R]_{0,diss}$ is the fraction that follows the dissociative first order route and $[R]_{0,inert}$ is the fraction that does not react at all.

4. Measurement of Nanoparticle Temperature by Raman Thermometry

We measured the electron temperature of the nanoparticle by the method promoted by Boerigter et al.³ In short, photons can scatter from the Fermi-Dirac distributed electrons in the nanoparticle. This gives a smooth inverse exponential background in the anti-Stokes Raman signal. Following their procedure, we fitted the anti-Stokes background by:

$$I_{aS,background} = I_{aS,0} \left[e^{E_{Raman}/k_B T} + 1 \right]^{-1} \quad (\text{S11})$$

To separate the background from the Raman signal of the adsorbate molecules, we used an approach inspired by the PolyMod algorithm by Lieber and Madhadevan-Jansen⁴. The basic idea of this algorithm is to fit a model-function to the data, and subsequently replace all data points whose value is larger than the fitted function value, by the function value. The thus obtained new dataset is then again fitted by the model-function and the replacement step is repeated. This procedure is repeated until a fitted function that only represents the background

remains. In the original PolyMod algorithm, a polynomial is used as model function. For the temperature determination, we used instead the function described in equation S11.

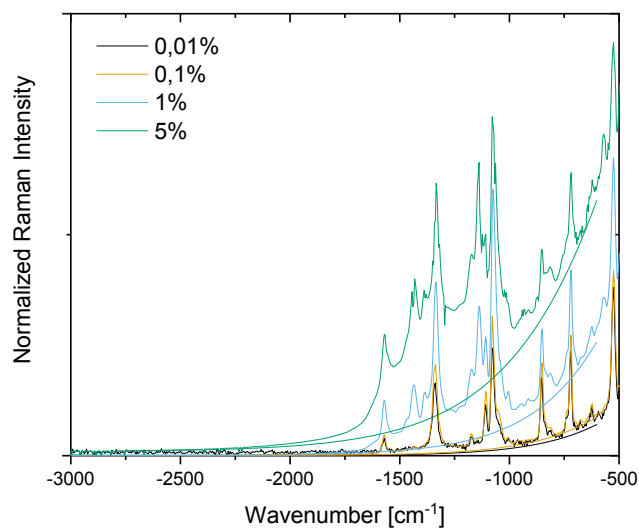


Figure S2. Anti-Stokes spectra at 4 different laser intensities and corresponding fits of the Fermi-Dirac background.

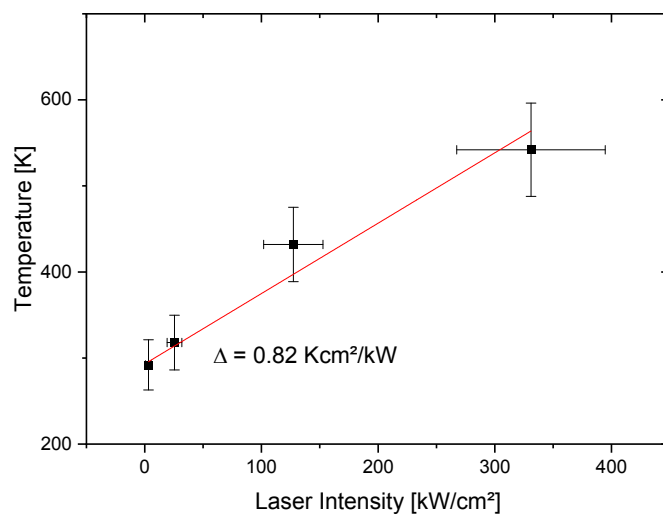


Figure S3. Particle temperatures extracted from anti-Stokes background versus the applied laser intensity. The linear fit has a fixed y-axis intercept at room temperature (20°C).

References

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- 2 P. W. Atkins and J. de Paula, *Atkins' physical chemistry*, Oxford University Press, Oxford, 2014.
- 3 C. Boerigter, U. Aslam and S. Linic, Mechanism of Charge Transfer from Plasmonic Nanostructures to Chemically Attached Materials, *ACS nano*, 2016, **10**, 6108–6115.
- 4 C. A. Lieber and A. Mahadevan-Jansen, Automated method for subtraction of fluorescence from biological Raman spectra, *Applied spectroscopy*, 2003, **57**, 1363–1367.