On the Role of Valence Band States and Plasmonic Enhancement in Electron Transfer Induced Transformation of Nitrothiophenol

Robin Schürmann,[a,b] Kenny Ebel,[a,b] Christophe Nicolas,[c] Aleksandar R. Milosavljević,[c] and Ilko Bald*[a,b]

[a] Physical Chemistry, Institute of Chemistry, University of Potsdam Karl-Liebknecht-Str. 24-25, 14476 Potsdam-Golm, Germany

[b] Department of Analytical Chemistry BAM, Federal Institute of Material Research and Testing Richard-Willstätter-Str. 11, 12489 Berlin, Germany

[c] Synchrotron SOLEIL L’Orme des Merisiers, Saint Aubin, BP 48, 91192 Gif-sur-Yvette Cedex, France

Experimental section:

Chemicals:
Trisodium citrate, HAuCl₄ and NTP have been purchased from Sigma Aldrich (Germany) and have been used without further purification. All Glassware was cleaned with aqua regia in advance and all chemicals were diluted in MilliQ filtered water.

AuNP synthesis:
The citrate stabilized AuNPs have been synthesized with a modified Turkevish method ¹. Briefly, 19.6 ml of 1 % HAuCl₄ has been dissolved in 480 ml MilliQ filtered water. The solution was rigorously...

¹ Turkevish, S. L.; Wightman, L. T. J. Am. Chem. Soc. 1960, 82, 583-584.
stirred and heated up in a 1 l three neck round bottom flask to a rolling boil under reflux using an oil bath (T_{oil}=125 °C). Subsequently, 5 ml of 0.475 M trisodium citrate solution was added rapidly using a syringe and the solution has been boiled for 20 more minutes and let cool down to room temperature. The AuNP solution was stored at 4°C.

AuNP characterization:

In order to determine the size distribution of the AuNPs, 2 µl AuNPs solution, washed with MilliQ filtered water, was dried on a freshly cleaved mica substrate. AFM measurements have been performed using a Flex-AFM from Nanosurf equipped with Tap150 Cantilevers (Force constant: 5 N/m. Resonance frequency: 150 kHz). The height of the NPs on the substrate was determined using the Gwyddion 2.48 software. UV-Vis spectra of the synthesized AuNP solution have been recorded with a Nanodrop 2000 from Thermo scientific.

SI 1: a) Size distribution of AuNPs determined from AFM images. Bimodal distribution is caused by aggregation during the drying process. b) Extinction spectra of two different batches of AuNPs after the synthesis.

SERS substrate preparation:

0.5 ml AuNP were incubated with 1 µM NTP overnight. Subsequently, the AuNPs were centrifuged trice (4000g, 5min) through a 0.5 ml Amicon filter (100 kDa) and refilled with MilliQ filtered water. After a final centrifugation the solution a 10 µl droplet was dried on a Si wafer (cleaned with acetone and MilliQ water and etched for 5min in a plasma oven in advance).

Raman measurements:

The Raman measurements have been performed with a Witec alpha 300 confocal Raman microscope equipped with four lasers with the wavelengths of 488 nm, 532 nm, 633 nm and 785 nm, respectively using a 600 lines/mm grid and a 50x objective (Nikon E-Plan, NA = 0.75). The laser power was determined using a FieldMax II power meter (Coherent) after the objective.

Dark field spectroscopy:

Dark field spectra have been recorded using a 50x Zeiss EC Epiplan HD objective (NA = 0.75) in the Witec alpha 300. The spectrum of the LED lamp has been recorded on a clean Si chip taking into account the reflectivity of the Si. The normalized scattering intensity has been determined by:
\[ I_{\text{norm}} = \frac{I_{\text{sample}} - I_{\text{dark}}}{I_{\text{lamp}} - I_{\text{dark}}} \]  

(SI1)

Reaction rates:

The observed reaction rate \( k_{\text{obs}} \) after an illumination time \( t \) for the transformation of NTP to DMAB can be determined from the intensity \( I_{\text{NTP}} \) and \( I_{\text{DMAB}} \) of the SERS signals of NTP and DMAB, respectively:

\[
\frac{dI_{\text{NTP}}(t)}{dt} = -k_{\text{obs}}(t) \cdot I_{\text{NTP}}(t) \quad (\text{SI2})
\]

\[
\frac{dI_{\text{DMAB}}(t)}{dt} = k_{\text{obs}}(t) \cdot I_{\text{NTP}}(t) \quad (\text{SI3})
\]

The initial intensities of \( I_{\text{NTP}} \) and \( I_{\text{DMAB}} \) are given by:

\[
I_{\text{DMAB}}(t = 0) = 0 \quad (\text{SI4})
\]

\[
I_{\text{NTP}}(t = 0) = I_{\text{NTP}}^0 \quad (\text{SI5})
\]

Thus, we can write the intensity \( I(t) \) by using formula SI2-SI5 and the final DMAB intensity \( I_{\text{DMAB}}^\infty \) as:

\[
I_{\text{DMAB}}(t) = I_{\text{DMAB}}^\infty \cdot (1 - e^{-k_{\text{obs}}(t) \cdot t}) \quad (\text{SI6})
\]

\[
I_{\text{NTP}}(t) = I_{\text{NTP}}^0 \cdot e^{-k_{\text{obs}}(t) \cdot t} \quad (\text{SI7})
\]

The ratio of \( I_{\text{NTP}}(t) \) and \( I_{\text{DMAB}}(t) \) is consequently given by:

\[
\frac{I_{\text{DMAB}}(t)}{I_{\text{NTP}}(t)} = \frac{I_{\text{DMAB}}^\infty}{I_{\text{NTP}}^0} \cdot (e^{k_{\text{obs}}(t) \cdot t} - 1) \quad (\text{SI8})
\]

We assume:

\[
I_{\text{NTP}}^0 = I_{\text{DMAB}}^\infty \quad (\text{SI9})
\]

hence, we can determine \( k_{\text{obs}} \) by using

\[
k_{\text{obs}} = \frac{\ln(1 + I_{\text{DMAB}}/I_{\text{NTP}})}{t} \quad (\text{SI10})
\]

from the measured Raman intensities.
SI 2: Observed reaction rates at 1s plotted as a function of the laser power for different laser wavelengths (Data presented in Figure 2 d)). Error bars are given from the standard deviation of three to five independent measurements. Data fitted with a power law function $k_{ob} = a \cdot I_{Laser}^N$ and the error is given by the fit.

Ligand exchange:

The citrate capping of the AuNPs was exchanged to NTP by adding 3 ml of 10 mM NTP solution to a 300 ml AuNPs solution and let it incubate overnight. Subsequently, the AuNPs have been washed by several steps of spin filtration (each 10 min at 3000g) using Millipore Amicon Filters (15 ml 30 kDa). After each centrifugation step the solution was refilled to its initial volume. In the final centrifugation step the concentration of the AuNPs was adjusted to 2 mM (in terms of Au atoms).

Synchrotron XPS:

The XPS measurements have been performed at the PLEIADES beamline at the synchrotron SOLEIL, which provides soft x-ray photons with a high intensity and energy resolution. In order to record XPS spectra of NP clusters in the gas phase, the multi-purpose source chamber (MPSC) of the beamline has been used. The details of the setup have been described elsewhere. Briefly, a beam of nanoparticle clusters was generated by using an atomizer (TSI Inc. 3076) with Ar at 35 Psi as carrier gas. The solvent (water) was removed by passing a desiccator and the size distribution of the NP clusters has been determined in parallel by differential mobility analysis (DMA) using a scanning mobility particle sizer (TSI 3008003).
SI 3: Differential mobility analysis of NTP capped AuNPs at an Ar pressure of 35 Psi.

The beam was introduced into the vacuum and focused by a set of aerodynamic lenses. At the entrance of the VG Scienta R4000 hemispherical electron energy analyzer the NP- and photon-beam were crossed to generate photoelectrons. In order to determine the total electron yields in the X-ray absorption measurements an electron yields detector was also mounted in the detector chamber. For the alignment of the particle beam SiNPs were used, which have been already studied recently. The photo absorption spectra of CO$_2$, N$_2$ and Xe gas have been recorded around the energy of certain electronic transitions in order to calibrate the PE (see SI 4 and Table 1).

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SI 4: X-ray absorption spectra: a) at the O1s edge of CO$_2$, b) at the N1s edge of N$_2$, c) at the 3d$_{5/2}$-6s transition of Xe, d) at the 4p-6s transition of Xe.

| Transition | Energy (eV) | Edges recorded |
|------------|-------------|----------------|
| Xe4p$^{5}$-6s of Xe | 141.55$^{5}$ | Valence band states |
| N1s-π$^{*}$ of N$_2$ | 400,865$^{6}$ | C 1s |
| O1s-π$^{*}$ of CO$_2$ | 535.0$^{7}$ | N 1s |
| Xe3d$_{5/2}$-6p of Xe | 674.00$^{6}$ | Au 4f, O1s, (N 1s), S2p |
**SI Table 1**: Values for the X-ray absorption of Xe, N$_2$ and CO$_2$ reported previously.

The ionization and Auger signals of the Ar carrier gas have been used to calibrate the electron energy. Therefore, electron energy of the ionization edges of the 2s, 2p, 3s and 3p states as well as the Auger electrons with an energy between 190 and 210 eV of the Argon carrier gas has been recorded using a photon energy of 674.0 eV, which was calibrated by the Xe3d$_{5/2}$-6p transition of Xe gas. The measured KEs have been plotted against the expected KEs (see SI 5) to obtain the calibration curve.

**SI 5**: a) XPS spectrum of the Ar carrier gas, recorded with a PE of 674.00 eV, showing the 2s, 2p, 3s and 3p edge as well as several Auger peaks. b) Measured KE of the photoelectrons measured as a function of the expected values for KE. Linear fit has been used to calibrate KE.

The origin of the signals, i.e. whether they come from the NP beam or from molecules is the gas phase can be differentiated by the 2d XPS spectra using the Scienta hemispherical analyzer in transmission mode (see SI 6).
SI 6: a) 2D XPS spectrum of NTP capped AuNP beam (top) and the respective spectrum integrated over all pixels (bottom) recorded using a PE of 674.00 eV. Electrons originating from the central part of the beam are imaged onto the central part of the 2D image. Since the diameter of the focused NP beam is typically smaller than the imaging area of the electron analyzer the signal of the beam can be seen in the center region of the 2D image. The Ar carrier gas and solvent molecules are not focused by the aerodynamic lens system and in consequence their photoelectrons fill the whole vertical area of the detector.

b) 2D XPS spectrum (top) and the respective integrated spectrum (bottom) showing the valance band region recorded using a PE of 141.55 eV.

XPS spectra from NTP ligands on AuNPs:

All XPS spectra are shown in Figure SI 7.

O 1s: At the O1s edge two peaks are observable (see SI6 a)). The larger peak at 539.9 eV originates from gaseous water and the shoulder at 537.2 eV is assigned to the NO$_2$ group of the NTP. The work function corrected binding energy of the NTP peak is given by 532.6 eV, which agrees well with the values described in the literature.

S 2p: Since the thiol group of NTP binds most likely to the AuNP surface, the photoelectrons need to pass at least the benzene rings and the NO$_2$ group of the NTP on their way to the detector. Consequently, a photon energy of 674.0 eV has been chosen to increase the mean free path of the electrons. Due to the lower cross section of S and lower photon flux at this photon energy, only a weak peak is observed at 166.6 eV, which corresponds to a work function corrected binding energy of 162 eV and can be assigned to the Au-S bond.

C 1s: Most of the peaks in the C1s spectrum need to be assigned to electrons, which might originate from Auger cascades of the Ar carrier gas. However, at a work function corrected BE of 284.6 eV a signal from the NP beam is observed, which can be assigned to the sp$^2$ carbon species of the benzene ring. Further contributions of carbon species with higher binding energies overlap with the Ar signals.

N 1s: The N1s signal of the NO$_2$ group typically has a binding energy of 406 eV, thus the signal would be expected around 410.6 eV due to the shift by the work function. As the N1s signal of residual N$_2$ gas in the chamber is located at 409.9 eV, the two contribution of the peak at 410.2 eV cannot be separated adequately.
SI 7: XPS spectra of NTP capped AuNPs recorded at the a) O1s (PE = 674.00 eV; Total energy resolution = 1.3 eV), b) S2p (PE = 674.00 eV; Total energy resolution = 1.7 eV), c) C1s (PE = 400,865 eV; Total energy resolution = 0.9 eV) and d) N1s (PE = 535.0 eV; Total energy resolution = 1.7 eV) edge. All spectra have been corrected with a Shirley type background. Due to the comparably low signal to noise ratio of the S2p signal, the S2p 1/2 and the S2p 3/2 cannot be resolved separately and are consequently fitted with a single peak, which is approximately 1 eV broader than the KE resolution.

XPS spectra from Citrate ligands on AuNPs:

SI 8: XPS spectra of citrate capped AuNPs recorded at the a) Au4f edge (PE = 674.00 eV; Total energy resolution = 1.7 eV) and b) C1s edge (PE = 400,865 eV; Total energy resolution = 0.9 eV) and c) the valence band states (PE = 141,55 eV; Total energy resolution = 0.2 eV)

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