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

Robin Schürmann, †‡ Kenny Ebel, †‡ Christophe Nicolas, § Aleksandar R. Milosavljević, § and Ilko Bald‡, †‡, §

†Physical Chemistry, Institute of Chemistry, University of Potsdam, Karl-Liebknecht-Str. 24-25, 14476 Potsdam-Golm, Germany
‡Department of Analytical Chemistry BAM, Federal Institute of Material Research and Testing, Richard-Willstätter-Str. 11, 12489 Berlin, Germany
§Synchrotron SOLEIL, L’Orme des Merisiers, Saint Aubin, BP 48, 91192 Gif-sur-Yvette, France

Supporting Information

Localised surface plasmon resonances (LSPRs) strongly enhance the electric field in the vicinity of illuminated noble-metal nanoparticles (NPs), which enables versatile applications from sensing to catalysis. In surface-enhanced Raman scattering (SERS), the increased near field in the vicinity of the NP surface is exploited to strongly enhance the inelastically scattered light of adsorbed molecules and consequently enhance the Raman signal by several orders of magnitude. Moreover, chemical reactions of the adsorbed molecules can be mediated by the LSPRs. One typical reaction mechanism is the transfer of a "hot electron", which is generated by the nonradiative decay of an LSPR. Alternatively, a direct electron transfer from the hybridized states of the valence band of the NPs and the adsorbed molecules to the unoccupied molecular orbitals of the ligand molecules is likely. The transformations from 4-aminothiophenol (ATP) or 4-nitrothiophenol (NTP), respectively, to 4,4-dimercaptosotiazobenzene (DMAB) are two of the most prominent plasmon-mediated reactions studied with SERS and tip-enhanced Raman scattering and typically serve as model reactions. Using SERS, the dimerization of NTP can be tracked; however, the transformation to DMAB is rather complex, involving the transfer of four electrons per NTP molecule and several chemical equilibria. Furthermore, the influence of thermal and electron-induced effects triggering the reaction has been controversially discussed. Nevertheless, according to recent studies, a predominant role of the hot carriers in plasmonic catalysis is assumed. Moreover, the metal band structure in plasmonic devices crucially determines the transport of hot carriers. Within the present work, the influence of accessible valence band states on the reaction rates of the hot-electron-induced conversion of NTP is elucidated. Therefore, SERS is used as a method to monitor the plasmon-mediated reactions in real time.

To fabricate a substrate for reproducible SERS measurements, a droplet of highly concentrated NTP-capped AuNPs (10 nm diameter) has been deposited on a freshly cleaned Si substrate. Besides the typical core-shell structures, relatively uniform areas of AuNPs have been formed during the drying process (see Figure 1a). Atomic force microscopy (AFM) images of these areas show flat AuNP multilayer structures with a quadratic surface roughness of ~3 nm (see Figure 1b). In Figure 1c, a Raman image of the NTP signal at 1337 cm⁻¹ is presented, which is assigned to the NO₂ symmetric stretching vibration, revealing very homogeneous and well-reproducible images of these areas show...
The Journal of Physical Chemistry Letters

nonirradiated spots with almost identical reaction conditions can be addressed with the confocal microscope. The dark-field scattering spectrum (see Figure 1d) shows the characteristics of a plain gold surface with strong scattering in the red and near-infrared regions and a comparably low scattering in the blue and green regions of the visible light, which confirms the formation of homogeneous NP films.

In Figure 2a, time-dependent Raman measurements on the substrate are shown, which reveal a decrease in the Raman signals assigned to NTP with ongoing illumination time and an increase in new Raman bands assigned to the formation of DMAB

\[
2\text{NTP} + 8\text{e}^- + 4\text{H}_2 \rightarrow 4\text{H}_2\text{O} + \text{DMAB}
\]  

(1)

The NTP NO2 stretching vibration at the 1337 cm\(^{-1}\) and 1445 cm\(^{-1}\) bands of the ag modes of DMAB\(^{15}\) have been used to track the reaction (see Figure 2b). On the basis of the ratio of these two signals, the observed reaction rate \(k_{\text{obs}}\) after an illumination time \(t\) can be determined (see the SI for details)

\[
k_{\text{obs}} = \ln(1 + \frac{I_{1445\text{cm}^{-1}}}{I_{1337\text{cm}^{-1}}})/t
\]

(2)

To rule out the influences of the desorption of the analytes and laser-induced modifications of the AuNP substrate, especially at high laser powers, it is important to determine the reaction rates using the ratio of the Raman bands. In Figure 2c, \(k_{\text{obs}}\) is shown as a function of \(t\), revealing a decrease following a power law. The time dependency of the reaction rate is caused by the inhomogeneous spatial distribution of the plasmonic enhancement on the nanoscale, as in the places with the highest field enhancement, the hot electrons are primarily generated;\(^{26}\) consequently, plasmon-mediated reactions preferably take place in these hot spots.\(^{27}\) The local reaction rate is given by

\[
\text{local reaction rate} = k \cdot [\text{NTP}] 
\]

(3)

where [NTP] is the concentration of NTP at a certain position on the plasmonic substrate, \([\text{e}^-]\) is the local hot electron generation rate, and \(k\) is the reaction constant, which remains obscure when the reaction kinetics is studied with SERS. The generation rate of hot electrons is assumed to be time-independent, and thus the local reaction rate can be described by pseudo-first-order kinetics. Because the observed Raman signal is a summation over many hot spots, the observed reaction rate decreases with time, as the molecules that mainly contribute to the signal experience the highest rates. Previous kinetics studies of the dimerization of NTP\(^{13,15}\) mainly did not take the influence of the inhomogeneity of the plasmonic enhancement into account, and hence the significance of the determined reaction constants and reaction orders is limited. van Schrojenstein Lantman et al. presented an approach to isolate the reaction taking place in the plasmonic hot spot from the bulk reaction of the molecules; however, a comparison of measurements under different reaction conditions is difficult with this method.\(^{14}\) In the present study, the required time-independent reaction parameters, which allow at least a qualitative comparison of measurements under different reaction conditions, are obtained by applying fractal-like kinetics,\(^{28}\) which has already been previously used to describe hot-electron-induced reactions.\(^{29}\) The time-dependent reaction rate is given by

\[
k_{\text{obs}} = k_1 \cdot t^{-h}
\]

(4)

where \(k_1\) is the rate constant at a time \(t = 1\) s and \(h\) is the fractal dimension of the system. The power law behavior of \(k_{\text{obs}}\) most likely originates from the Pareto distribution of the plasmonic enhancement of coupled noble-metal NPs.\(^{30}\) The reaction rates have been recorded at different laser wavelengths and powers, as shown in Figure 2d. Typically, the reaction rate should follow a power law where the exponent is given by the number of involved photons \(N\)\(^{31}\)

DOI: 10.1021/acs.jpclett.9b00848
Because four electrons are involved in the transformation from NTP to DMAB (see eq 1), \( N \) is expected to be 4. A value close to 4 has only been observed for the measurements using light with a wavelength of 633 nm \( (N = 4.7 \pm 0.8) \) for the investigated laser powers (fitted presented in SI 2). For other excitation wavelengths, \( N \) is clearly smaller than 4; however, because the reaction involves several chemical equilibria\(^{36}\) and is influenced by thermal and nonthermal effects, the exact dependency on the laser power is supposed to be rather complex.\(^{37}\) At higher laser powers, the increase in the reaction rate is less pronounced due to a trade-off with the thermally induced back reaction.\(^{33}\) Overall, the highest reaction rates at a given laser power have been observed for illumination with 488 and 532 nm light, even though the plasmonic enhancement is comparably low in this wavelength region (Figure 1d). Nevertheless, for 785 nm laser light, where the plasmonic enhancement is the highest, the reaction rate is significantly higher than that for 633 nm light. Recent studies suggest that the reaction rates of hot-electron-induced reactions correlate with the dark-field scattering of the AuNP–substrate,\(^{38}\) but the dependency of the reaction rates on the photon energy presented here can obviously not be explained solely by the plasmonic response of the substrate.

To monitor the electronic states of the AuNP/NTP system available for the electron-transfer-induced reaction, XPS measurements of isolated AuNPs clusters have been performed at the PLEIADES beamline of the synchrotron SOLEIL.\(^{35,37}\) In the setup, a focused beam of NP clusters is crossed with a tunable soft X-ray beam under vacuum, and the kinetic energy (KE) of the generated photoelectron has been determined with an electron energy analyzer.\(^{39}\) By using a beam of AuNPs in the gas phase instead of AuNPs deposited on a solid substrate, X-ray-induced damage of NTP is avoided.\(^{35}\) Details of the experimental setup are presented in the SI. In brief, the NTP-capped AuNPs have been brought to the gas phase by an atomizer, and the size of the generated clusters prior to entering the ultra-high vacuum (UHV) chamber has been determined by differential mobility analysis, revealing a maximum of the size distribution at \( \sim150 \) nm (see SI 3).\(^{38}\) The binding of the NTP on the AuNPs has been validated by the C 1s, N 1s, O 1s, and S 2p XPS spectra of the NP clusters (see SI 7). The absolute zero position and the linearity of the photoelectron KE scale have been calibrated according to the reference of the BE is \( \Phi = -\Phi_v \) (highlighted in the box in Figure 3b). In the Fermi energy (highlighted in Figure 3b). In the Fermi energy (highlighted in Figure 3b). In the Fermi energy (highlighted in Figure 3b). In the Fermi energy (highlighted in Figure 3b). In the Fermi energy (highlighted in Figure 3b). In the Fermi energy (highlighted in Figure 3b). In the Fermi energy (highlighted in Figure 3b). In the Fermi energy (highlighted in Figure 3b).

\[
k_1 \propto I_{\text{laser}}^N \tag{5}
\]

Because our NP beam is free-standing, all of the binding energies measured in the experiment are referenced to the vacuum level. Those binding energies will be noted with an index “v”. To determine the work function of the NTP-capped AuNP clusters, the Au 4f spectra have been recorded using a photon energy of 674.00 eV to get a sufficiently high escape depth of the photoelectrons to pass the capping molecules (see Figure 3a). The Au 4f\(\text{v}\) peak of the Au\(^0\) was determined to be at a \( \text{BE}_v \) of 88.4 \( \pm \) 0.3 eV, which is shifted by \( (4.6 \pm 0.5) \) eV according to the values previously reported, which were measured with respect to the Fermi level in the solid state.\(^{34}\) (The uncertainty is given by the mean square root of the uncertainty of the KE, the fitting error, and the variation of values reported in the literature.) The difference of the BE is attributed to the work function of the AuNP clusters (see eq 5). Typically, the work function of AuNPs is \( \sim5.3 \) eV;\(^{35}\) however, already due to the presence of a few layers of water, the work function can be shifted by 0.8 eV toward lower electron energies.\(^{46}\) A similar decrease in the work function has been previously observed due to the adsorption of thiophenol derivatives on copper surfaces.\(^{47}\) We have determined the work function of citrate-capped AuNPs to be \( (4.2 \pm 0.5) \) eV (see SI 8).

In addition to the core-level states of the NTP-capped AuNPs, the valence band states of the system have been recorded using a PE of 141.55 eV (see Figure 3b). With the knowledge of the work function, the recorded valence band states can also be discussed with respect to the Fermi level. The gaseous water state at \( \text{BE}_v \) = 12.6 eV from gas-phase water is used to validate the energy calibration of the KE of the photoelectrons. (c) Zoom-in of the valence band states. Colored lines mark the photon energies of the Raman laser with respect to \( E_p \).

\[
\Phi = \text{PE} - \text{BE} - \text{KE} \tag{6}
\]
The Journal of Physical Chemistry Letters

which is relevant for the light-mediated transformation of NTP to DMAB, the electron counts increase with higher BEs. The onset of the valence band structure is in accordance with previous studies of AuNPs with thiol-bound ligand molecules and reflects the local density of occupied states in our system. The electron counts at 2.6 eV with respect to the Fermi level (indicated by the blue line in Figure 3c, corresponding to 488 nm excitation) are higher compared with those at 1.6 eV (indicated by the dark-red line in Figure 3c, corresponding to 785 nm excitation) by a factor of ~3. The transition probability of an electron is proportional to the density of occupied states.19 Because the transfer of four electrons for each NTP molecule is required for the conversion to DMAB, the increase in the density of occupied states leads to an increase in the transition probability by almost two orders of magnitude. Furthermore, the LUMO of NTP adsorbed on a gold surface is expected to be located 2 eV above E_F.23 Hence, also the density of accessible unoccupied states increases when going from 785 to 488 nm excitation. An electron transfer into the low-energy onset of the LUMO is already possible at low photon energy (785 nm), but, in general, the transfer probability significantly increases with higher photon energies due to the higher density of both unoccupied molecular states and occupied NP states.

In Scheme 1, an energy diagram of the electronic initial and final states involved in the electron transfer from the AuNPs to the NTP molecules is sketched together with the photons of different wavelengths and plasmonic enhancements triggering the reaction. The higher density of accessible electronic states for photons with wavelengths of 488 (2.6 eV) and 532 nm (2.33 eV) compared with photons with longer wavelengths can qualitatively explain the high observed reaction rates, taking into account that four photons/electrons are involved in the process (see eq 5).

A direct electron transfer is advantageous for the higher photon energies used here for the SERS measurements (see colored lines in Figure 3c); however, besides the electronic initial and final states, also the work function and the local density of photons determine the electron-transfer probability. In consequence, the higher reaction rates using 785 nm compared with 633 nm laser light can most likely be explained by taking into account the strong plasmonic enhancement of the substrate in the near-infrared region, which increases the local photon density in this wavelength regime.

In summary, it is demonstrated that the dependency of the reaction rates of the plasmon-mediated transformation of NTP to DMAB on the excitation laser wavelength cannot be fully explained by the plasmonic response of the substrate. Moreover, the accessible electronic states of the NP–ligand system need to be considered to explain the reaction kinetics. Nevertheless, to derive a complete understanding of the kinetics in plasmon-catalyzed reactions in the future, further knowledge of the unoccupied state of the system and a real-time monitoring of all intermediate states are required. These findings will be crucial, on the one hand, to optimize plasmonic catalytic systems and, on the other hand, to find conditions for sensing applications, where the signal enhancement is high while unwanted electron-induced reactions are widely suppressed.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcl.9b00848.

Experimental section, XPS spectra from NTP ligands on AuNPs, XPS spectra from citrate ligands on AuNPs (PDF)

AUTHOR INFORMATION

Corresponding Author
E-mail: bald@uni-potsdam.de.

ORCID
Aleksandar R. Milosavljević: 0000-0003-3541-8872
Ilko Bald: 0000-0002-6683-5065

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research is supported by the European Research Council (ERC; consolidator grant no. 772752). We acknowledge beamtime at the synchrotron SOLEIL through project 20171359. We thank Stephan Sass for his support in the synthesis of the AuNPs.

REFERENCES


(25) Huang, Y.-F.; Zhu, H.-P.; Liu, G.-K.; Xie, W.-Y.; Ren, B.; Tian, Z.-Q. When the signal is not from the original molecule to be detected: Chemical transformation of para-aminothiophenol on Ag during the SERS measurement. J. Am. Chem. Soc. 2010, 132, 9244–9246.


