

Photoswitching in Azobenzene-Functionalized Self-Assembled Monolayers on Au

Insplorion's Nanoplasmonic Sensing (NPS) technology enables measurements of the photoisomerization kinetics of self-assembled monolayers of azobenzene-containing thiols in real time. In this application note it is shown how quantitative data on the photoinduced trans–cis and cis–trans isomerization processes in inert gas atmosphere was obtained as a function of irradiation intensity.

Introduction

Functional surfaces, i.e., surfaces that respond to external stimuli (e.g., light, electric potential or current, redox reactions, or ion (pH) concentration) in a defined manner are of interest for applications in e.g. data storage, sensors, and molecular machines. Such systems are commonly prepared by self-assembly of functional molecules onto appropriate substrates. Azobenzene derivatives are one of the most frequently studied classes of switchable compounds. The azobenzene functionality exhibits cis–trans isomerism. The thermodynamically stable trans isomer can be converted to the cis isomer by irradiation with UV light of ~ 365 nm. Back-isomerization to the trans isomer occurs upon irradiation with blue light of ~ 435 nm or thermal relaxation. Here it is shown how NPS can be used to obtain quantitative data on the photoisomerization kinetics of azobenzene-containing thiol SAMs.

Experimental Procedure

Insplorion bare gold sensors were cleaned in UV/O₃,

followed by an O₂ plasma and then rinsed in MilliQ water before immersing them in a solution of the azobenzene-containing 3-(4-(4-hexyl-phenylazo)-phenoxy)-propane-1-thiol in dichloromethane. After allowing the thiols to adsorb for 30 min, the sensors were rinsed in dichloromethane, dried under nitrogen gas and directly mounted in the measurement chamber, which was purged with nitrogen gas during the measurement. An UV LED at 365 nm and a blue LED at 455 ± 10 nm at variable intensities up to ~ 10 mW

cm^{-2} were used for photoswitching of the molecules.

Results

In Figure 2a a real-time measurement of the NPS wavelength of a thiol SAM is shown. A shift of the NPS signal of ca. 0.04 nm is seen upon switching between the cis and trans conformational states of the azobenzene moieties in the SAM. Although the photoinduced changes in the resonance wavelength λ_{LSPR} are small, they are clearly larger than the noise (ca. ± 0.01 nm).

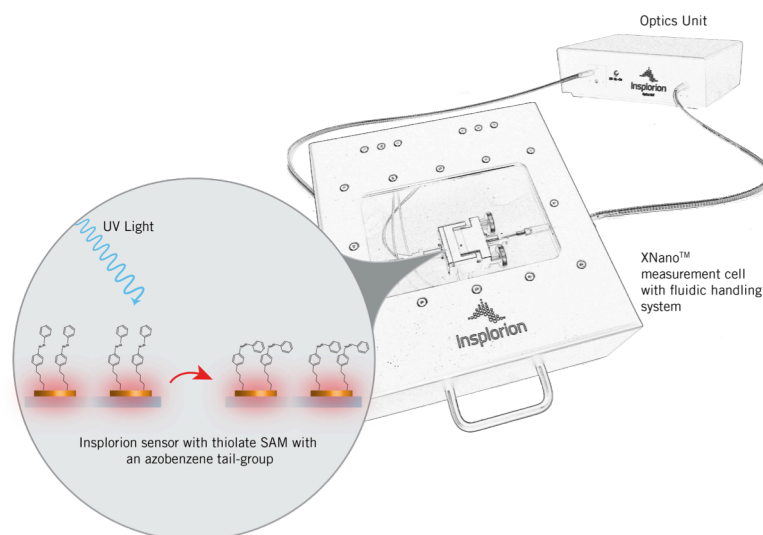


Figure 1: Insplorion system setup. The inset shows a schematic illustration of the sensors and molecules used in this application example (not to scale!).

A)

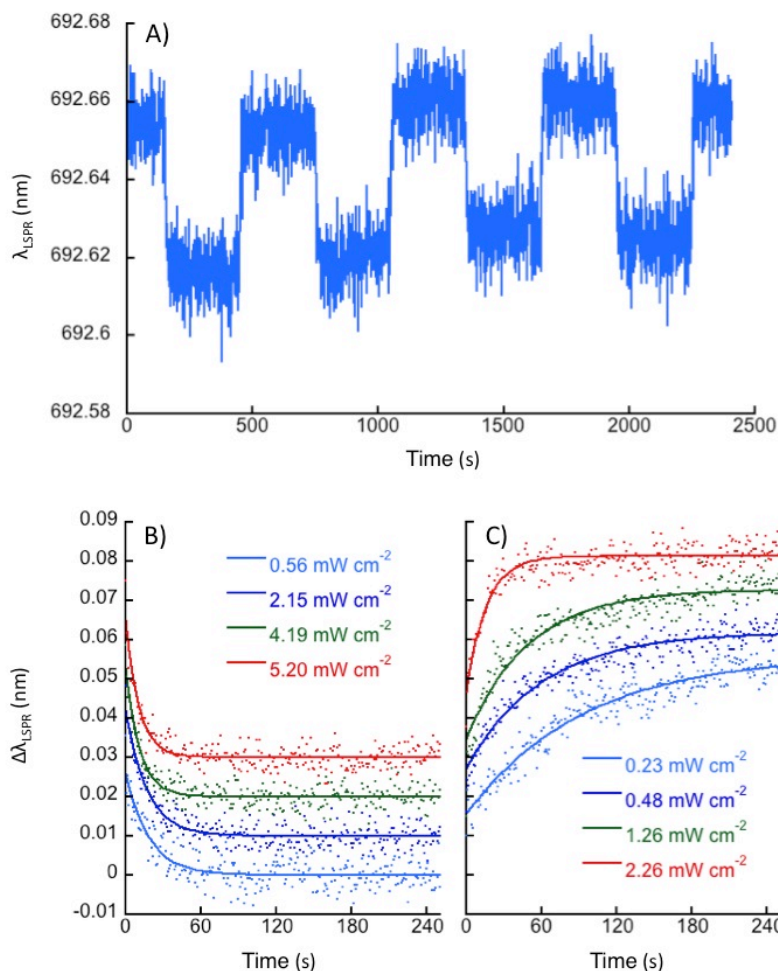


Figure 2: (A) Photoinduced variations of the NPS wavelength for a SAM upon irradiation with UV light (365 nm, 2.15 mW cm⁻²) and blue light (455 nm, 2.26 mW cm⁻²) at room temperature. (B,C) Irradiation intensity dependence of the averaged variations (typically 5 switching events) for the (B) trans-cis and (C) cis-trans photoisomerization at room temperature.

The photoswitching kinetics was investigated for different intensities of the switching light. For the quantitative analysis of the

isomerization kinetics, multiple data sets (typically 5) were averaged. The LSPR transients, $\Delta\lambda_{LSPR}(t)$, for the trans-cis and cis-trans

transitions, respectively, are shown in figure 2b,c for different irradiation intensities. The reactions were found to follow first-order kinetics. The isomerization rate constants k , obtained for different irradiation intensities, by exponential fitting to the data, are presented in table 1. k was found to increase with increasing light intensity, as expected. The total NPS signal shift, $\Delta\lambda_{LSPR,max}$, between the trans and cis states does not exhibit a significant dependence on the irradiation intensity in agreement with simple first order transitions in a two state system.

Conclusions

Inspilorion's nanoplasmonic sensing technology was applied to study photoswitching reactions of azobenzene-containing thiol SAMs. The high sensitivity of the NPS technology allowed the very small changes in the SAMs to be monitored in situ and in real time.

Table 1: Rate constants for the trans-cis and cis-trans isomerizations of the azobenzene-containing thiol.

Trans-Cis, 365 nm		Cis-Trans, 455 nm	
Irradiation intensity (mW/cm ²)	Rate constant, k (s ⁻¹)	Irradiation intensity (mW/cm ²)	Rate constant, k (s ⁻¹)
0.56	0.0534±0.0048	0.23	0.0173±0.0012
2.15	0.0590±0.0036	0.48	0.0377±0.0022
4.19	0.0900±0.0059	1.26	0.0685±0.0037
5.20	0.0952±0.0061	2.26	0.0900±0.0060

References

[1] *Localized Surface Plasmon Resonance Investigation of Photoswitching in Azobenzene-Functionalized Self-Assembled Monolayers on Au*, Mathias Müller et al., *Langmuir* 29 (2013) 10693-10699.