

# Dye Molecule Interactions with Flat Dye Sensitized Solar Cell $\text{TiO}_2$ Photoelectrode Mimics

## Introduction

In this application note, based on experiments performed in collaboration with Prof. Michaël Grätzel at EPFL in Switzerland, Indirect Nanoplasmonic Sensing (INPS) is for the first time applied to study dye molecule adsorption on flat, thin (12-70 nm) and dense (i.e. non-porous)  $\text{TiO}_2$  films.

## The INPS Technology

The INPS sensor consists of plasmonic Au nanodisks (typical dimensions of 80-200 nm in diameter and 20 nm in height) deposited on a glass substrate and covered by a thin (up to a few tens of nm) dielectric spacer layer. This spacer layer (i) enables tailoring of the surface chemistry of the INPS sensor chip, (ii) protects the Au nanodisks from

the environment, and (iii) prevents structural re-shaping of the nanodisks.

In the experiments presented here dye molecules adsorbing on the sensor chip surface locally change the refractive index within the strongly enhanced electromagnetic field region (i.e. the sensing volume) of the localized plasmon excitation in the Au nanodisks. This induces a spectral shift of the plasmon extinction peak, which is used as the readout.

## Experimental

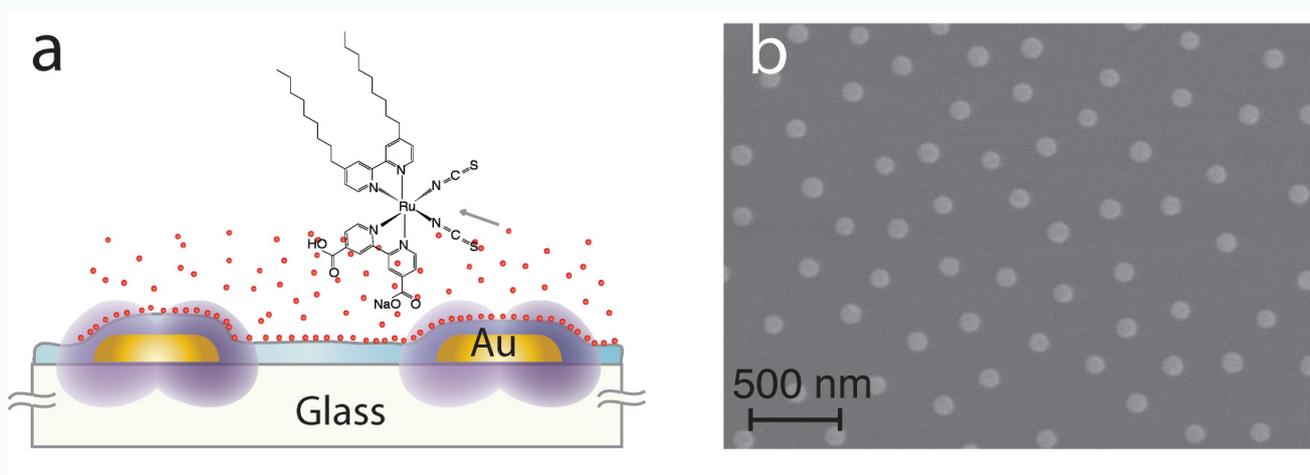
The INPS sensors used here consist of Au nanodisks (average diameter 110 nm, height 20 nm) deposited on a glass substrate and covered by a thin (12-70 nm) RF-sputtered  $\text{TiO}_2$  film (Fig. 1a,b).

The sample was then mounted in a liquid phase measurement cell (Insplorion XNano prototype) and exposed to a Ru dye Z907 solution under continuous white-light illumination in a transmission configuration. The spectrally resolved extinction of the light was monitored and analyzed in real time using the Insplorer® software.

As a complementary readout, the standard optical absorbance signal from the dye was measured simultaneously.

## Results

The plasmon resonance peak of the Au nanodisks shifts to the red (compared to air) when the sample is exposed to the solvent (Fig. 2a) and further red-shifts in the dye solution



**Figure 1:** (a) Schematic illustration of the used INPS sensor chip structure comprising a 12 - 70 nm thick dense  $\text{TiO}_2$  film on top of the Au sensor nanodisks. The red dots indicate the adsorbed dye molecules. Also indicated is the chemical structure of the used Ru-dye Z907. (b) SEM image of the used INPS sensor covered with a 12 nm thin dense  $\text{TiO}_2$  film.



(Fig. 2b). The latter shift is attributed to dye molecule adsorption on the  $\text{TiO}_2$  surface.

The complete dye adsorption experiment consists of two sequential dye exposures up to near monolayer saturation, each followed by a rinsing step in pure solvent. During the course of the measurement, the temporal evolution of the plasmon peak position is monitored (Fig. 2c). The initial red-shift of the plasmon peak position by 1.6 nm is attributed to adsorption of dye molecules onto the  $\text{TiO}_2$  layer. The subsequent smaller blue-shift of 0.3 nm upon rinsing is attributed to desorption of a minor fraction of dye molecules that are reversibly bound, e.g., in aggregated form or at more weakly bound sites.

By repeating the dense film experiment with systematic variation of the thickness of the  $\text{TiO}_2$  film, the spatial extension of the sensing volume of the INPS sensor was found to be ca. 70 nm from the Au nanoparticle sensor surface into and above the  $\text{TiO}_2$  film.

## Conclusions

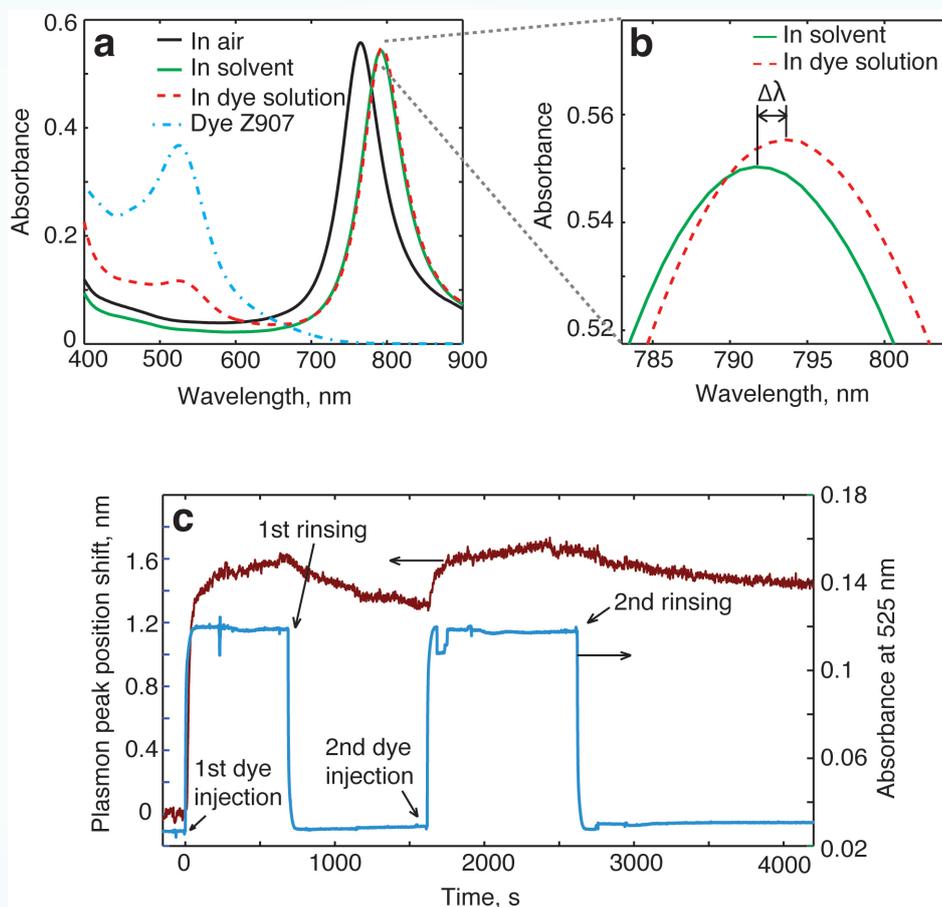
Real-time kinetics measurements of dye molecule adsorption on dense  $\text{TiO}_2$  films, mimicking DSSC photoelectrodes, were performed for the first time using Insplorion's INPS technology.

These results demonstrate the potential of the INPS platform to obtain new insights into the adsorption dynamics of molecular species from

the liquid phase onto the surface of solid materials.

## References

*Time-Resolved Indirect Nanoplasmonic Sensing Spectroscopy of Dye Molecule Interactions with Dense and Mesoporous  $\text{TiO}_2$  Films*, Viktoria Gusak, Leo-Philipp Heiniger, Michael Graetzel, Christoph Langhammer, and Bengt Kasemo, *Nano Letters* (2012) dx.doi.org/10.1021/nl3003842.



**Figure 2:** (a) Absorbance spectra of an INPS sample with a 12 nm  $\text{TiO}_2$  film measured: in air (black curve), in solvent (green), and in dye solution (red, dashed) after completion of the dye adsorption. The absorbance spectrum of the Z907 dye solution is also displayed (blue, dashed-dotted). The latter was measured at a higher dye concentration than the one used for the INPS measurements, in order to better display the spectral features. The peak absorbance value at 525 nm was used to follow injection and removal of dye molecules into/from the bulk liquid. (b) Zoomed-in spectra of the plasmon resonance peak in solvent and in dye solution. The spectral shift, denoted  $\Delta\lambda$ , is the quantity used to follow dye adsorption/desorption events on the  $\text{TiO}_2$  samples. (c) Temporal evolution of the plasmon peak position shift (red curve), and absorbance at 525 nm (in blue) in a dye adsorption kinetics measurement.

