Nanoplasmonic Sensing of Dye Diffusion in Mesoporous TiO_2

Insplorion's Localized Surface Plasmon Resonance (LSPR) technology enables in situ, real-time kinetics measurements of small molecule percolation and adsorption into thick mesoporous structures by probing the hidden internal interface. Both kinetic and quantitative (i.e. diffusion coefficient and surface coverage) information can be derived.

Introduction

A Dye Sensitized Solar Cell (DSSC) exploits few micrometers thick mesoporous TiO_2 films impregnated with light-absorbing dye molecules as photoelectrode. The adsorption and percolation kinetics of dye impregnation is an important parameter in optimisation and production of DSSCs. Knowledge and control of this process is thus key to enhance the overall DSSC efficiency and to maximise reproducibility for industrial manufacture. Our nanoplasmonic sensing technology provides critical quantitative real-time *in situ* data for understanding and optimisation of the dye impregnation process.

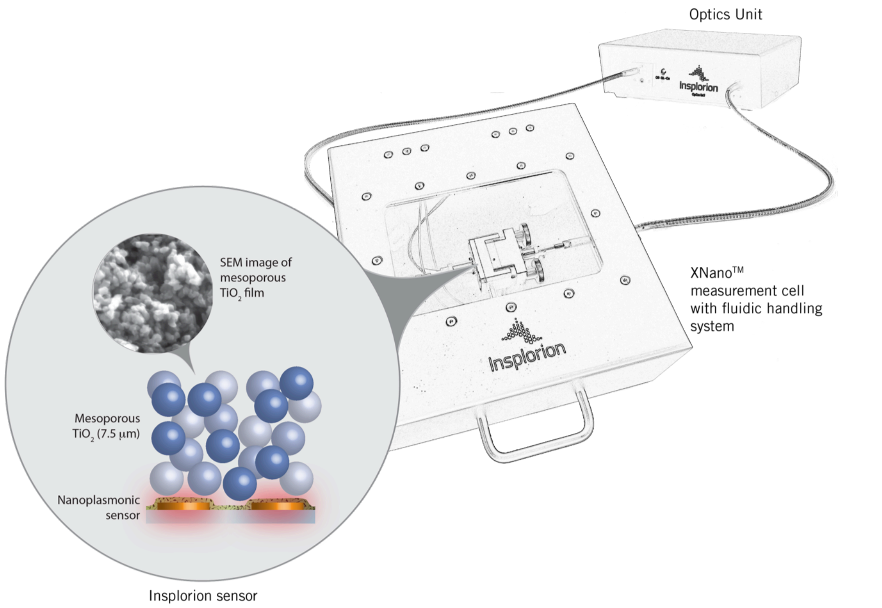

Figure 1: Insplorion system setup. The inset shows a schematic illustration of the sensor used in this application example (not to scale!).

Experimental Procedure

The several micrometers thick mesoporous TiO_2 film was screen-printed onto Insplorion sensors pre-coated with a thin TiO_2 adhesion layer. The sensors were then sintered at 500°C for 1 hour in air. One sensor at a time was then placed in the measurement cell into which solvent and dye solution was injected by means of the liquid handling system. During a measurement, both the LSPR signal from the sensor located at the *hidden internal interface* of the mesoporous TiO_2 layer, and the dye absorbance (at 525 nm) were monitored in real time.

Results

Upon injection of dye molecules there is an immediate shift in the absorbance at 525 nm caused by light absorption of the dye molecules. This shift is proportional to the *total* amount of dye in the light path, i.e. present both inside the mesoporous TiO_2 film and in the solution above it. Once the dye molecules have reached the *hidden internal interface* of the mesoporous film, where the plasmonic sensing *locally* takes place, there is an increase in the LSPR signal reflecting the amount of dye adsorbed at this interface. Typically, there is a significant time-delay between dye injection and the onset of LSPR signal, reflecting the time it takes for the dye molecules to reach the hidden interface. From this experiment it is possible to follow the dye molecule penetration rate into the mesoporous TiO_2 film in real time (Figure 2).
Figure 3A shows the measured dependence of the dye percolation time t_p (the delay time between dye injection into the measurement cell and onset of LSPR

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signal) on TiO_2 thickness, L.

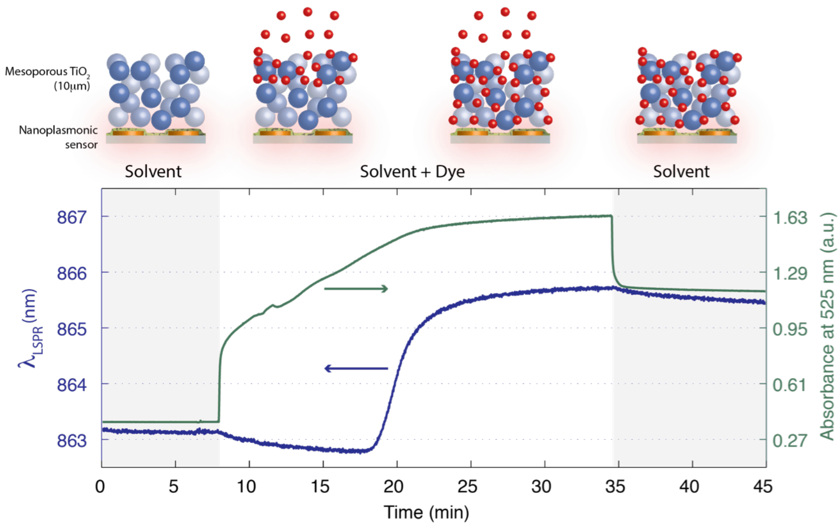

Figure 2: The LSPR signal (blue curve) and dye absorbance (green curve) during a typical dye diffusion experiment. The *time delay* between onset of the absorbance signal and the LSPR signal indicates the total diffusion time of dye molecules through the mesoporous layer.

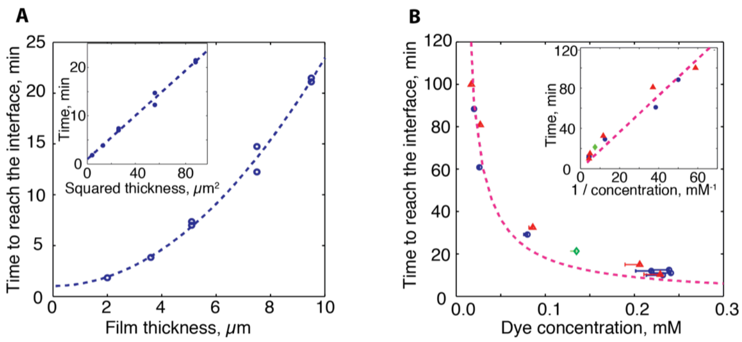

Figure 3: Time to reach the hidden interface of the mesoporous TiO2 film (A) as a function of the film thickness at fixed dye concentration and (B) as a function of the dye solution concentration for constant TiO2 thickness. The dashed lines are least square fits to the experimental points based on an analytical diffusion front model derived in the original paper by Gusak et al.

Clearly t_p follows a theoretically predicted L^2 dependence very well. From a least-square fit (dashed line) of the model to the experimental points one can estimate the effective diffusion coefficient, D^*, of the dye molecules inside the mesoporous layer since the film thicknesses and the dye solution concentration are known. A value of D^* = 9.9 μm²/s for dye Z907 inside the mesoporous TiO_2 in a 1:1 mixture of acetonitrile and tert-butanol was found.

The dependence of t_p on the dye solution concentration, c_0, at constant sample thickness can also be investigated. These results are shown in Figure 3B. Again, the experimental data points fit very well to the $t_p \sim 1/c_0$ dependence predicted by the analytical model derived by Gusak et al. The value of D^* obtained from the best fit to the data points in Figure 3B is 13.5 μm²/s. This is, in view of the made approximations and experimental error bars, reasonably close to the value of 9.9 μm²/s obtained from the thickness dependence measurements discussed above.

Conclusions

Insplorion's nanoplasmonic sensing technology is a unique method for studying diffusion and adsorption of molecules in porous films. The extreme local sensitivity of the Insplorion technology enables probing the internal hidden interface of a thick film. This enables accurate and high-resolution measurements of the percolation time of small molecules into thick porous structures. From this time, the effective diffusion coefficient of the molecules in the pores can be derived.

This study was originally performed by researchers at the Department of Applied Physics, Chalmers University of Technology, Sweden, in collaboration with Prof. Michaël Grätzel's group at the Laboratory of Photonics and Interfaces at Ecole Polytechnique Fédérale de Lausanne, Switzerland.

References

[1] *Diffusion and Adsorption of Dye Molecules in Meso-porous TiO_2 Photoelectrodes Studied by Indirect Nano-plasmonic Sensing.* V. Gusak, L. Heiniger, V. P. Zhdanov, M. Grätzel, B. Kasemo, and C. Langhammer, *Energy Environ. Sci.*, 2013, DOI: 10.1039/C3EE42352B.