

# **Real Time Adsorption and Desorption Kinetics of Dye Z907 on a Flat Mimic of Dye-Sensitized Solar Cell TiO<sub>2</sub> Photoelectrodes**

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## Abstract

A dye molecule monolayer formed on a  $\text{TiO}_2$  surface is a key component in dye sensitized solar cells. It is usually formed by adsorbing dye molecules from a solution. The dye layer should absorb as much solar light as possible and convert the light to photoelectrons, injected into the  $\text{TiO}_2$  conduction band. For that purpose the dye molecules should adsorb on  $\text{TiO}_2$  with appropriate molecular orientation and close packing. We measured adsorption and desorption kinetics of dye Z907 on thin compact  $\text{TiO}_2$  films *in real time* using Indirect Nanoplasmonic Sensing (INPS). From kinetic curves, we derived adsorption and desorption rate constants in a direct way, which has not been done for such systems previously. Subsequently, we derived the equilibrium adsorption constant from both kinetics (by the ratio of the adsorption and desorption rate constants) and from a measured Langmuir isotherm obtained experimentally using the same method, the same sample and the same experiment. The two values are in reasonably good agreement considering possible error sources and our approach thus constitutes an effective way of determining more reliable equilibrium constants for dye –  $\text{TiO}_2$  systems. Furthermore, by measuring a series of intermittent adsorption-desorption steps, we found successively less desorption at a given coverage after each rinsing step, and conclude that there are different binding states and that re-organization of the dye molecules on the  $\text{TiO}_2$  surface occurs over rather long timescales. The rearrangement process seems to accelerate by intermittent rinsing and associated desorption of loosely bound molecules. The results suggest that the detailed conditions for the dye impregnation kinetics can be used to optimize the dye layer.

## **Keywords**

Nanoplasmonic sensing, dye sensitized solar cell, DSC, Langmuir isotherm, equilibrium rate constant, rearrangement.

## **Introduction**

Adsorption of organic dye molecules onto inorganic surfaces is an important process for many applications, the most prominent one being dye-sensitized solar cells (DSCs).<sup>1</sup> Photodegradation of organic pollutants using photocatalysis<sup>2</sup> is a second example. In a DSC, dye molecules are adsorbed in a densely packed monolayer on the surfaces of nanoparticles of a wide-band gap semiconductor, often  $\text{TiO}_2$ . The nanoparticles constitute a mesoporous structure, with electrical contact between the typically 20 nm large particles and with empty space between them. The dye molecules perform the function of harvesting sunlight, which leads to generation of excited electrons that are rapidly injected into the  $\text{TiO}_2$  conduction band. After injection they diffuse through the mesoporous  $\text{TiO}_2$  film to the collecting electrode and the external circuit, where they perform work. An excited electron from a dye molecule, injected into the  $\text{TiO}_2$ , is immediately replaced into the ground (HOMO) state by another electron from a redox couple electrolyte, into which the dye- $\text{TiO}_2$  system is immersed. In this way, the electric circuit is closed, and the system functions as a solar cell.

In the complex DSC system, the dye monolayer plays a central role and the scrutiny and optimization of its formation is therefore critical to further advances of DSCs. Optimal performance of a DSC demands that the layer of dye molecules on the  $\text{TiO}_2$  surface fulfills a number of requirements (sometimes not

totally compatible so that compromises may have to be made). First, in order to absorb as much solar light as possible, the number of dye molecules per unit volume should be maximized. Second, since only those molecules that form a chemical bond of the right type with the  $\text{TiO}_2$  can inject electrons into its conduction band, the dye molecules should adsorb in a monolayer with the correct molecular orientation and chemical bonding. More correctly, the electronic coupling/overlap between the excited dye state and the  $\text{TiO}_2$  conduction band should be large enough to allow fast electron transfer, suppressing other decay routes. For example, if the molecules are adsorbed in multilayers, the ones on top of the first monolayer will absorb light and increase the density of light absorbers, but without generating any useful charge carriers. Third, there are indications that a densely packed dye layer provides an efficient barrier for undesirable charge recombination between the  $\text{TiO}_2$  and the electrolyte. A detailed critical discussion of this mechanism can be found in the work by O'Regan *et al.*<sup>3</sup> Finally, in addition to the above-mentioned properties, the dye monolayer on  $\text{TiO}_2$  should also be stable toward desorption into the electrolyte to support long-time stability of the device. In light of the above it is obvious that methods to monitor and evaluate the dye adsorption/deposition/impregnation process *in real time* are highly desirable in order to optimize the dye monolayer.

During manufacture, the dye layer is deposited on a  $\text{TiO}_2$  surface by adsorbing molecules, from a dye solution in an organic solvent, onto a previously formed mesoporous structure. The important processes involved in the adlayer formation are adsorption, desorption and diffusion (through the mesoporous

structure). One property that reflects the combined effect of these processes is how the dye loading (or coverage) on the  $\text{TiO}_2$  depends on the dye concentration in the bulk solution and on exposure times. This has been studied for mesoporous films of the kind used in DSCs,<sup>4-7</sup> and also for model systems of single crystals of  $\text{TiO}_2$ <sup>8</sup> and thin compact  $\text{TiO}_2$  films.<sup>9</sup> There is, however, only little work available on adsorption and desorption kinetics of dye molecules on  $\text{TiO}_2$  surfaces studied in *real time*, i.e., to the best of our knowledge, only a recent Quartz crystal microbalance (QCM) study<sup>9</sup> and our own initial study using indirect nanoplasmonic sensing (INPS).<sup>10</sup>

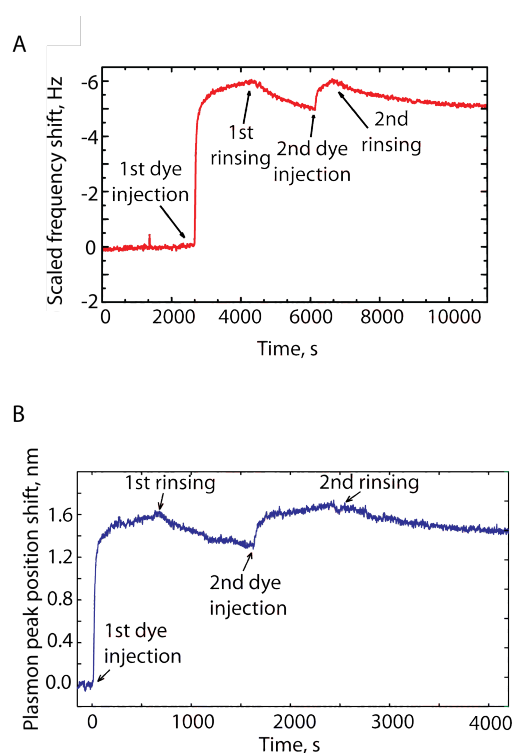


Figure 1. QCM-D (A) (from reference 6) and INPS (B) data (from reference 7) showing dye uptake on flat  $\text{TiO}_2$  versus time, during dye exposure interrupted by rinsing with solvent. The data clearly show desorption upon rinsing with solvent,

*fast recovery of the lost coverage upon the next dye exposure and a successively slower desorption after an exposure-rinsing cycle. Note that the time scale are not perfectly matched for the two experiments – the picture is shown to illustrate that the two methods QCM-D and LSPR/INPS yield very similar results.*

Here we investigated in detail the adsorption and desorption of dye Z907 on thin compact TiO<sub>2</sub> films produced by Atomic Layer Deposition (ALD) by real time kinetics measurements using our INPS technique.<sup>11</sup> Specifically, from the INPS measurements, we extracted for the first time the values of the adsorption and desorption rate constants by direct use of the obtained kinetics data. The found ratio of these values, *i.e.* the equilibrium adsorption constant, agrees reasonably well with the one extracted from the Langmuir isotherm, relying on analysis of the equilibrium coverage for different dye concentrations in solution. Despite the observed agreement, we also find that the Langmuir model as such does have a limited applicability to the system under study. For this purpose we performed a series of three adsorption-desorption (rinsing) cycles and observed less desorption after each sequential rinsing step. The Langmuir model does not account for such behavior, which implies that there are different ways of binding of dye molecules to the TiO<sub>2</sub> and that the relative fraction of the different binding states changes during adsorption and/or with elapsed time. This also points to the possibility of using variations of adsorption – rinsing/desorption sequences to optimize the adsorbed dye layer.

## **Experimental methods**

The Indirect Nanoplasmonic Sensing (INPS) technique<sup>11</sup> was used to follow adsorption and desorption of dye molecules on polycrystalline, flat TiO<sub>2</sub> films in real time. The technique is based on the phenomenon of localized surface plasmon resonance (LSPR), which occurs in metal nanostructures of sizes smaller than the wavelength of light. The oscillating electric field of light incident on a metal nanoparticle couples to collective oscillations of the conduction electrons in the nanoparticle, which causes enhanced absorption and scattering. This occurs at particular energies for a given particle size, shape and material. The resonance manifests itself as a peak in extinction of light passing the particles. Important for sensing applications is (i) that the electric field generated in the nano-proximity of the metal nanoparticle is strongly enhanced and (ii) that the energy (or wavelength) at which LSPR occurs depends on the dielectric function of the surrounding medium. When the dielectric properties change (due to, for example, a molecule arriving close to the nanoparticle surface), the wavelength of the LSP resonance shifts, thus enabling to sense events that lead to a change in the dielectric properties of the medium. The sensitivity to dielectric changes near the nanoparticle is very high due to the enhanced electric field there, as demonstrated *e.g.* for measuring formation of a dye monolayer on a flat TiO<sub>2</sub> surface with fraction of a monolayer sensitivity (Ref. 10 and Figure 1). The sensitivity distance is short-ranged, typically within 100 nm from the nanoparticle surface,<sup>10</sup> which allows monitoring events locally, close to the surface of the sensor particle(s).

The INPS chips (Figure 2A), used for studying the adsorption and desorption kinetics, were round borofloat glass substrates (2.5 cm in diameter), covered

with a quasi-random pattern (no long-range order but a rather uniform nearest neighbor distance) of Au nanodiscs, each disc 150 nm in diameter and 20 nm high. The nanodiscs were fabricated by the hole-mask colloidal lithography process.<sup>12</sup> The chips were coated with a 10 nm TiO<sub>2</sub> film deposited by Atomic Layer Deposition (ALD) in a Cambridge Nanotech Savannah S100 system (Figure 2A). When dye molecules adsorb on the TiO<sub>2</sub> surface, replacing the solvent molecules, the dielectric function of the medium within the sensing distance of the Au nanoparticles changes, which leads to a shift in the plasmon resonance peak wavelength (Figure 2A). This shift is the main signal that was monitored in the present INPS measurements. Comparison between gravimetric data (QCM-D) and dye adsorption data on the same type of flat TiO<sub>2</sub> films has demonstrated proportionality between the plasmon resonance peak shift and dye molecule coverage.<sup>9-10</sup>

The plasmon resonance peak position of the coated sensors was at about 870 nm in the solvents, thus deliberately well separated from the dye absorbance, which sets on at about 800 nm and increases towards shorter wavelengths, with a maximum at around 525 nm. The sensor chips were mounted in a home-built flow cell, through which solvents and dye solutions were pumped using a peristaltic pump. Extinction spectra were continuously collected from an illuminated spot in the middle of the sample, using a fiber-coupled halogen lamp (AvaLight-HAL) and a spectrometer (AvaSpec-1048). A long-pass filter was used in combination with the lamp in order not to illuminate the dye molecules with visible light to minimize photobleaching and possibly other effects.



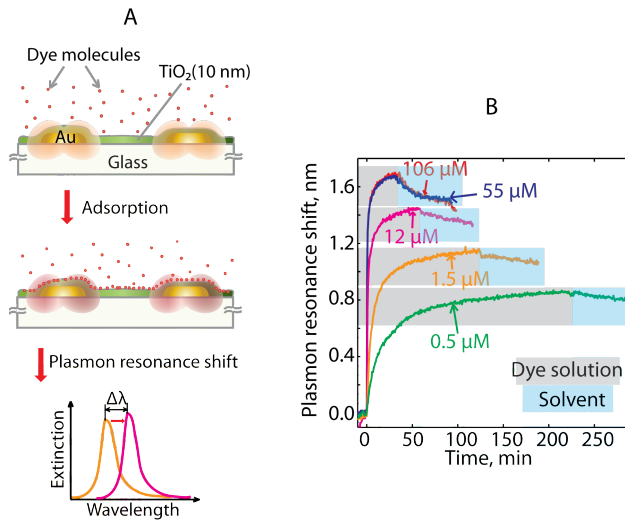
Dye Z907 powder was dissolved in either dimethyl sulfoxide (DMSO) or a 1:1 volume mixture of acetonitrile and tert-butanol, at concentrations specified in the main text. The solvents were purchased from Sigma-Aldrich (grades: DMSO >99.5%, MeCN 99.8%, tBuOH >99.7%) and used as received. The sensor chips were used about 10 times each and thoroughly cleaned in between the measurements. The cleaning was performed by soaking a chip in a 0.1 M solution of tetrabutylammonium hydroxide (TBAOH) in DMSO (30 min, 2 beakers), and rinsing in deionized water (30 min, 3 beakers) and with ethanol. Before each measurement, a chip was annealed at 400 °C in air for 30 min, and inserted into the cell immediately after having cooled to about 150 °C.

## **Results and discussion**

### *Determination of $K_{eq}$ from kinetics constants and the Langmuir isotherm*

Figure 2B shows the plasmon resonance peak shifts for five adsorption-desorption measurements done at different concentrations of dye Z907 in a 1:1 acetonitrile:tert-butanol mixture. The concentrations spanned two orders of magnitude, ranging from 0.5  $\mu$ M to 106  $\mu$ M. When the sensor is exposed to the dye solution, the plasmon peak red-shifts, indicating formation of a dye layer on the TiO<sub>2</sub> surface, since the dye molecules have a higher refractive index than the solvent molecules. The adsorption process first occurs at a fast rate, and then slows down (Figure 2B). Upon replacing the dye solution with pure solvent, the plasmon peak blue-shifts slightly, which corresponds to a fraction of dye molecules desorbing from the surface. We also note that the rate of desorption during post-exposure rinsing is higher after a short exposure at high

concentration compared to a long exposure at low concentration (compare the 106  $\mu\text{M}$  and 0.5  $\mu\text{M}$  curves).



*Figure 2. (A) The principle of the INPS technique. Upon adsorption of dye molecules on the TiO<sub>2</sub> film, the plasmon resonance shifts in wavelength, which is the signal that we monitored. (B) The plasmon resonance shift monitored in time, as the sensor is exposed to a dye solution (this stage is marked with gray boxes) and the pure solvent (blue boxes). Five concentrations were measured: 0.5  $\mu\text{M}$ , 1.5  $\mu\text{M}$ , 12  $\mu\text{M}$ , 55  $\mu\text{M}$ , and 106  $\mu\text{M}$ .*

In the following, we focus on the analysis of the adsorption and desorption kinetics using the framework of the Langmuir kinetic model. We chose this model because of its simplicity and pedagogical value, and also because adsorption of dyes on TiO<sub>2</sub> surfaces has been readily analyzed using the

Langmuir isotherm approach<sup>4-5, 8-9</sup> in the literature - in spite of its potential limitations.

Typically, in reported studies the final (equilibrium) loading of dye on TiO<sub>2</sub> surfaces as a function of dye concentration in solution is used to construct the Langmuir isotherm, which allows extracting the equilibrium adsorption constant. The simplest version of the model used for this purpose assumes that (i) the adsorption and desorption rates are first order, (ii) all adsorption sites are equivalent, (iii) each site can hold one or zero molecules, and (iv) the adsorbed molecules do not interact with each other. According to this model, the relative coverage  $\theta$  (*i.e.*, the fraction of sites on the surface that are occupied by adsorbed molecules) changes with time as:

$$\frac{d\theta}{dt} = k_a c(1 - \theta) - k_d \theta, \quad (1)$$

where  $k_a$  is the adsorption rate constant,  $c$  is the concentration of molecules in the solution, and  $k_d$  is the desorption rate constant. The plasmon peak shift in the INPS measurements is proportional to the amount of molecules adsorbed on the surface.<sup>13</sup> To convert the LSPR peak shift measured by INPS into surface coverage  $\theta$ , we assume that all available sites on the TiO<sub>2</sub> surface are occupied by dye molecules at the highest concentration used (about 0.1 mM), *i.e.*, that the monolayer is then saturated. This is a justified approximation, since desorption in the studied system is slow (although not negligible for some of the analysis). The corresponding plasmon peak shift at saturation was 1.7 nm (Figure 2B). Thus, by dividing all the kinetic curves by this value we converted the peak shift into the coverage  $\theta$ .

Equation (1) takes a particularly simple form when the coverage is very small, near  $\theta = 0$ , which corresponds to the initial stage of adsorption. In this case desorption is negligible and  $d\theta/dt = k_a c$ . Thus, by extracting the initial adsorption slopes  $d\theta/dt$  and plotting them versus the concentration, one can obtain the value of the adsorption rate constant  $k_a$ . We implement this for the initial stages of adsorption as shown in Figure 3A. The extracted initial adsorption slopes from these measurements and several additional ones are shown as a function of the concentration in Figure 3B. For the higher concentrations, the values of the slopes tend to level off (the inset in Figure 3B). This is an experimental artifact, related to the fact that it takes some time to exchange the liquids – specifically the solvent to the dye solution - in the measurement cell. In our case this time is about 10 s, and since the initial slopes of the two highest concentrations in Figure 3A were measured over 10 s, the actual concentration during this initial time was lower than its nominal value. This effect diminishes for the lower concentrations, when the exchange time of liquids in the measurement cell is fast compared with the kinetics. Therefore, we use the three lowest concentrations in order to extract the value of  $k_a$  from a linear fit to the initial slope  $k_a c$  as a function of the concentration (Figure 2B). This gives  $k_a = 1384 \text{ M}^{-1}\text{s}^{-1}$ .

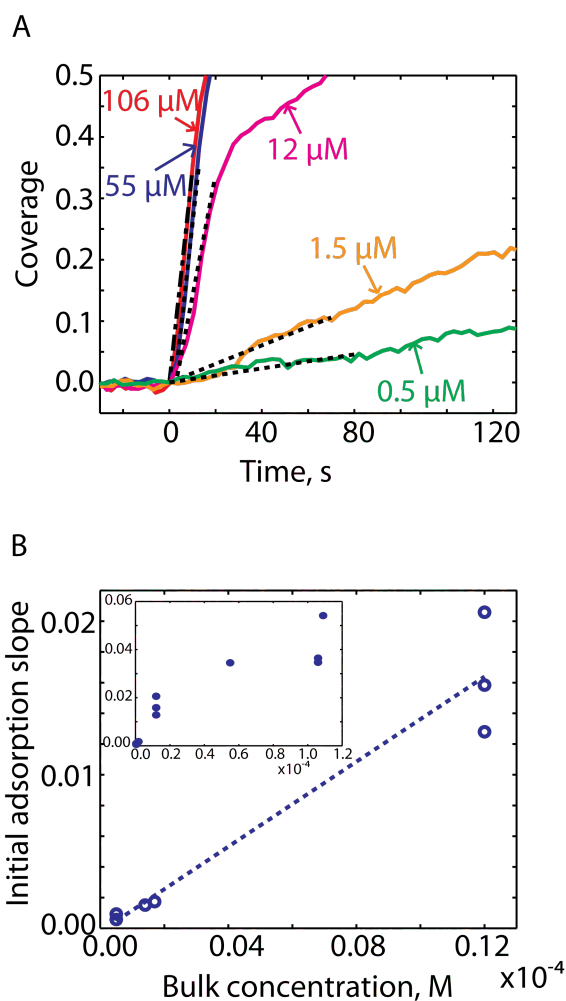


Figure 3. (A) Initial adsorption kinetics for the measurements from Figure 1B (note, however, that the plasmon peak shift has now been converted to surface coverage). The initial slopes are shown in black dashed lines. (B) Values of the initial adsorption slopes for the lowest concentrations, plotted versus the dye solution concentration (the values were extracted from the data in panel (A) and several additional measurements). The linear fit provides the value of  $k_a$ . The inset shows the values for all five concentrations used. For deriving  $k_a$ , we used only the lower concentrations, since for the two highest ones, the initial adsorption slope is influenced by the finite filling time of the measurement cell.

Equation (1) can also be simplified when there are no dye molecules present in the bulk liquid, *i.e.*, during rinsing with pure solvent. In this case  $c = 0$ , and  $d\theta/dt = -k_d\theta$ . The desorption rate constant  $k_d$  can thus be extracted from desorption slopes upon rinsing,  $d\theta/dt$ , plotted versus the coverage  $\theta$ , as shown in Figure 4A. The absolute values obtained are plotted versus the corresponding coverage at the beginning of desorption in Figure 4B. The slope of the linear fit corresponds to the desorption rate constant, and its value is  $k_d = 3.2 \cdot 10^{-4} \text{ s}^{-1}$ . The ratio  $k_a/k_d$  is the equilibrium adsorption constant  $K_{eq}$ , and using the obtained values of  $k_a$  and  $k_d$ , we get  $K_{eq} = 4.3 \cdot 10^6 \text{ M}^{-1}$ .

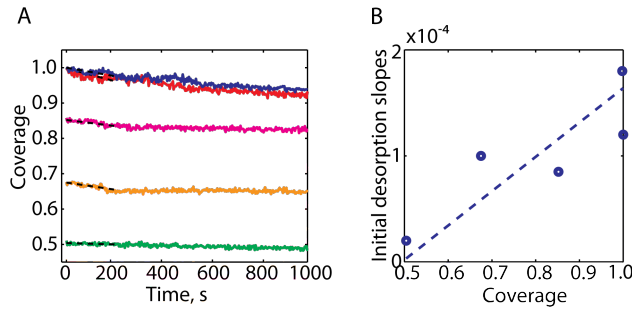


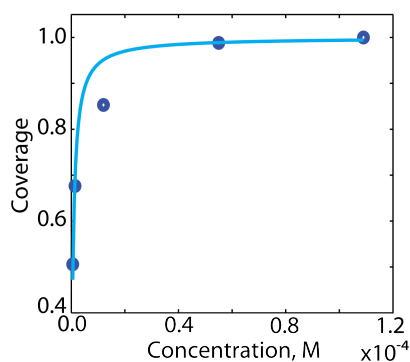
Figure 4. (A) Desorption kinetics from the measurements in Figure 1B, and the initial desorption slopes (black dashed lines). (B) Initial desorption slopes as a function of the coverage in the beginning of desorption (at  $t = 0$  in panel (A)). The linear fit provides the value of  $k_d$ .

Instead of the kinetic derivation of  $K_{eq}$  one can also obtain  $K_{eq}$  from a Langmuir isotherm, *i.e.*, from the dependence of the equilibrium coverage on the dye solution concentration, as typically done in the literature. However, one can see from Figure 2B that the adsorption in most of the measurements was not fully

saturated when the rinsing started. However, we expect this to be at least partly due to rearrangements of dye molecules on the surface, which occurs over long time scales, and not necessarily reflects the intrinsic time it takes to reach the equilibrium, as discussed in more detail later in the paper. An isotherm based on the values from Figure 2B is shown in Figure 5. It can be fitted with the Langmuir dependence

$$\theta = \frac{K_{\text{eq}}c}{1 + K_{\text{eq}}c}. \quad (2)$$

The obtained value of  $K_{\text{eq}}$  is  $1.6 \cdot 10^6 \text{ M}^{-1}$ . This agrees reasonably well with the value obtained by analyzing the initial adsorption and desorption kinetics directly, as described above ( $4.3 \cdot 10^6 \text{ M}^{-1}$ ).



*Figure 5. Adsorption isotherm based on measurements in Figure 2B, fitted with the Langmuir equation (2).*

The values of the rate constants obtained in this work ( $(2 - 4) \cdot 10^6 \text{ M}^{-1}$ ) are also in reasonably good agreement with those reported in the literature. Harms *et al.*<sup>9</sup> performed QCM-D measurements on a similar *compact* TiO<sub>2</sub> film surface

and the same dye, Z907, and obtained  $K_{eq}$  of  $5 \cdot 10^6 \text{ M}^{-1}$ . However, the equilibrium constants reported for *mesoporous nanocrystalline*  $\text{TiO}_2$  films are usually two orders of magnitude smaller. Fattori *et al.*<sup>5</sup> estimated  $K_{eq}$  to be  $4 \cdot 10^4 \text{ M}^{-1}$  from electrochemistry measurements for dye Z907 on mesoporous  $\text{TiO}_2$  films. Fillinger *et al.*<sup>4</sup> obtained  $K_{eq} = 3 \cdot 10^4 \text{ M}^{-1}$  for dye N3 on mesoporous  $\text{TiO}_2$  films, by measuring the amount of dye, which was forced to desorb from impregnated  $\text{TiO}_2$  films. Lu *et al.*<sup>8</sup> used photocurrent (IPCE) measurements to derive coverage of dye N3 on various single crystal  $\text{TiO}_2$  surfaces, and fitted a second stage of so-derived adsorption kinetics using the Langmuir model. They obtained  $k_a$  of  $40 - 1000 \text{ M}^{-1}\text{s}^{-1}$  for the different surfaces, where the upper range is similar to our value of  $1380 \text{ M}^{-1}\text{s}^{-1}$ . The desorption rate constant  $k_d$  ranged from  $4 \cdot 10^{-4}$  to  $3 \cdot 10^{-3} \text{ s}^{-1}$  in their work<sup>8</sup>, while the one in our work is  $3.2 \cdot 10^{-4} \text{ s}^{-1}$ .

These results reflect a wide spread of rate constant values presented in the literature. It is at this point therefore appropriate to comment on possible sources of errors in their determination. The derivation from kinetics (adsorption and desorption rate constants as done in our work) is commonly plagued by transport effects; during adsorption this means that the local concentration at the surface may initially be lower than the bulk concentration, due to diffusion limitations, and then the real  $c$  in equation (1) is smaller than the bulk concentration. This underestimates the real  $k_a$  value. During desorption the opposite applies - slow diffusion may lead to a non-zero bulk concentration near the surface during the initial phase of desorption, making it apparently slower than without such effects. This underestimates the  $k_d$  value and the two effects



partly compensate each other. However, the former influence is usually more severe. The  $K_{eq}$  value from kinetics may therefore be somewhat underestimated in our analysis. The  $K_{eq}$  value derived from the adsorption isotherm is not affected by the error sources caused by diffusion transport effects, since the system is in equilibrium. Here the uncertainty instead derives from the validity of the adsorption-desorption model used and from the uncertainty whether real equilibrium is reached or not before the dye exposure is interrupted/the coverage value measured. Considering these effects we consider the agreement between the kinetic and the thermodynamic  $K_{eq}$  values quite reasonable. Determining rate constants in two different ways (*i.e.*, by both the kinetic and the thermodynamic approaches) using one and the same technique and sample, as done in this work, is an important step towards reducing the impact of such effects and towards obtaining the correct  $K_{eq}$  value.

#### Effects of adsorption-rinsing/desorption cycles and deviation from the simple Langmuir model

The simple first order Langmuir model used above is likely to be an oversimplification of the real dye molecule -  $TiO_2$  surface interaction kinetics and thermodynamics. Indications for this are found both in our own results and in the literature. For example, as indicated above, rearrangements of dye molecules in the adsorbed layer over long time scales, affect the equilibrium coverage, and such effects are not contained in the model. This effect may actually also affect the  $K_{eq}$  value determined from kinetics since the phenomenon is of minor importance for the initial adsorption behavior ( $k_a$ ) but may affect  $k_d$ . Moreover, it has been pointed out<sup>4, 8, 14-15</sup> that the assumptions of equivalence of all

adsorption sites and absence of interactions between the dye molecules might not hold for the dye-TiO<sub>2</sub> system. Fillinger and Parkinson<sup>4</sup> impregnated mesoporous TiO<sub>2</sub> films with N3 dye for various exposure times, and using solutions of various concentrations, but kept the final dye loading similar for the different conditions. Noticeably, upon rinsing, they observed larger desorption of dye from samples impregnated using solutions of higher concentrations and during shorter times. The authors therefore suggested that adsorption occurs via a two-step process, where a less strongly bound state converts to a more strongly bound state<sup>4</sup>. In their interpretation, the dye molecules bind preferentially to TiO<sub>2</sub> with one carboxylate group at higher concentrations, while at lower concentrations, two carboxylate groups bind to the surface, which provides a stronger binding. Lu *et al.*<sup>8</sup> arrived at similar conclusions in their study of adsorption of the same dye molecule (N3) on single crystal TiO<sub>2</sub> surfaces. In line with these conclusions, Bazzan *et al.*<sup>14</sup> proposed a series of adsorption-desorption cycles that increased the dye (N719) loading of porous TiO<sub>2</sub> films and the corresponding solar cell efficiencies, supposedly by removing loosely bound molecules through desorption and thus improving the dye layer quality upon subsequent adsorption. In particular, after a series of such adsorption-desorption steps, the amount of desorbed dye decreased, while the dye loading increased.<sup>14</sup> Neale *et al.*<sup>15</sup> observed similar behavior for the same type of dye (N719). Some of our earlier studies<sup>7, 9-10</sup> actually indicated the presence of more than one possible adsorption state for dye Z907 on a TiO<sub>2</sub> surface. Both our initial INPS study<sup>10</sup> (which motivated the expansion into the present work) and QCM-D measurements<sup>9</sup> demonstrated a higher dye loading on compact TiO<sub>2</sub> films obtained after a rinsing and re-exposure to a dye solution

compared to a continuous dye exposure (Figure 1). Additional measurements of dye loading in mesoporous TiO<sub>2</sub> films<sup>7</sup> revealed a two-stage adsorption process, where the initial fast stage (tens of minutes) was followed by a much slower one (many hours). Both these results indicate re-arrangements of the dye layer on the TiO<sub>2</sub> surface that occur over long time scales, that seem to be enhanced by rinsing/desorption cycles, and that are not accounted for by the simple Langmuir model.

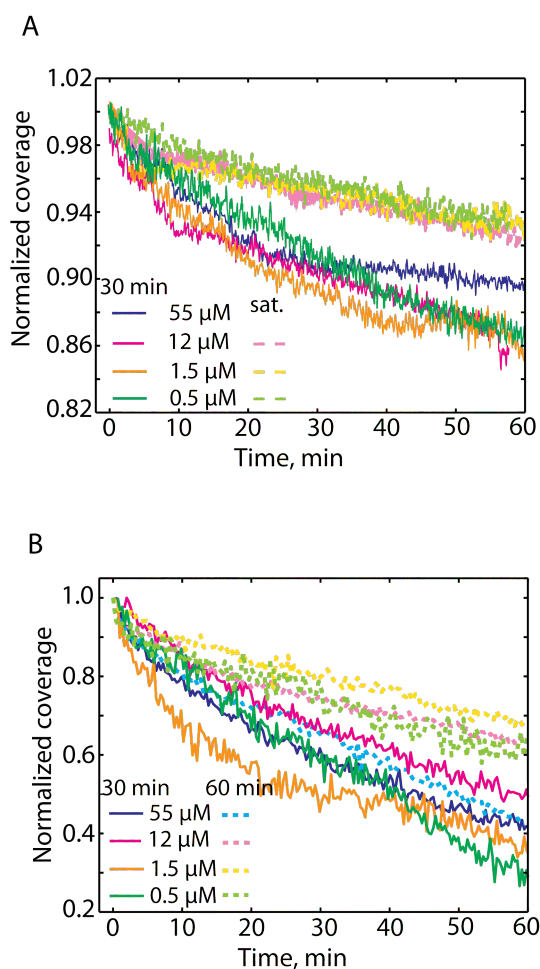


Figure 6. (A) Comparison of desorption kinetics in the 1:1 acetonitrile:tert-butanol mixture for films where adsorption was done up to "saturation" (the measurements from Figure 2B; marked "sat." in the label and represented by the upper three curves), and where adsorption was performed for 30 min (lower four curves). (B)

*Comparison of desorption kinetics in DMSO, occurring after adsorption during 30 min and 60 min, respectively.*

In the remaining part of this paper we therefore take a closer look at the desorption kinetics at different dye exposures and coverages to further elucidate the role of dye molecule rearrangements during the monolayer formation. Figure 6A shows desorption kinetics for measurements from Figure 2B and other similar measurements, where the adsorption step was interrupted after 30 min. The curves are here normalized so that the coverage in the beginning of the desorption steps is 1 and the y-axis shows the *fraction* of molecules that remain on the surface during desorption. In this type of plot there is no significant difference between desorption from samples where adsorption was done at different concentrations. However, one observes less desorption for measurements where the preceding adsorption step was longer in time; around 14% was desorbed after 1 hour for most measurements with a 30 min adsorption period, while about 7% desorbed after measurements with “saturated” adsorption. This difference supports the presence of a reorganization process, occurring slowly over long time scales in the adsorbed layer, *i.e.* where time, and not coverage or exposure, is the most important parameter.

To illustrate the role of the used solvent for the observed phenomena, we also investigated the desorption kinetics for a dye layer adsorbed from a solution in dimethyl sulfoxide (DMSO). Solutions of Z907 in DMSO are often used for impregnation of TiO<sub>2</sub> photoelectrodes in the DSC fabrication process, and the

solubility of this dye in DMSO is higher than in the acetonitrile:*tert*-butanol mixture. This means that the stability of the adsorbed dye layer in DMSO should be lower than in acetonitrile:*tert*-butanol. Figure 6B shows desorption of the Z907 in DMSO, for films where adsorption lasted for 30 min and for 60 min, respectively. The desorption is much more pronounced in DMSO compared to the other solvent; about 60% of dye was desorbed after a 60 min rinsing for the cases where the adsorption was 30 min long. However, when the adsorption lasted 60 min, desorption was less pronounced (*ca.* 40%), showing a similar process of reorganization as in the case of the acetonitrile:*tert*-butanol solvent.

To get further insight into the effect of time and/or rinsing on the properties of adsorbed dye layers and the reorganization process, we performed a series of intermittent adsorption/desorption measurements comprising three adsorption and desorption cycles for Z907 in the acetonitrile:*tert*-butanol mixture. Figure 7A,B shows such measurements for concentrations of 106  $\mu\text{M}$  and 15  $\mu\text{M}$ , where the adsorption steps lasted for about 10 min, and desorption (rinsing) stages were 30 min long. Measurements with corresponding *continuous* 30 min exposure (corresponding to the sum of the three adsorption steps for the intermittent measurements) to dye solution are also shown. The y-axis in Figure 7C,D shows the fraction of molecules that stayed on the surface as a function of rinsing time. For both concentrations, there seems to be less desorption after each subsequent adsorption-desorption cycle, although the difference in absolute coverage is small. This could be due to rinsing removing dye molecules that are not optimally bound, and leaving time and space on the surface for reorganization to occur, including creation of empty sites for adsorption of more

strongly bound molecules during a subsequent exposure to the dye solution. A similar behavior has been observed by other authors.<sup>4, 8, 10, 14-15</sup> Desorption after 30 min of continuous exposure lies initially close to the one after 10 min of exposure, although it levels off earlier than the latter for both concentrations. The fraction of molecules removed during desorption (under corresponding adsorption conditions) is somewhat smaller for the films where adsorption was done at the lower concentration. These observations again support the suggestion that dye molecules rearrange on the TiO<sub>2</sub> surface. During the generally slower adsorption process at lower concentrations, the dye molecules have more time to bind and rearrange before neighboring empty sites are occupied by additional molecules adsorbing from the solution. In other words, when adsorption is very fast, neighboring molecules may lock each other into local structures that on average correspond to a lower coverage and need long time or even solvent rinsing to rearrange into more densely packed structures.

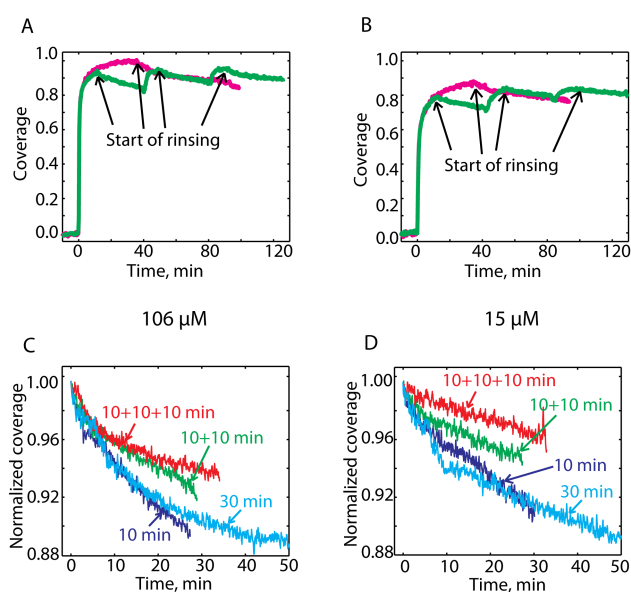


Figure 7. Three adsorption-desorption cycles, each adsorption lasting about 10 min, and desorption about 30 min, together with a 30 min long continuous adsorption. The measurements were performed for concentrations of 106  $\mu\text{M}$  (A, C) and 15  $\mu\text{M}$  (B, D) in 1:1 acetonitrile:tert-butanol solvent mixture. A and B show the evolution of the coverage in time. C and D show coverage, normalized to the one just before desorption was started, during each desorption step.

## Summary and Conclusions

In this work, we investigated adsorption and desorption kinetics for dye Z907 on thin compact  $\text{TiO}_2$  ALD films in real time, using the Indirect Nanoplasmonic Sensing (INPS) technique. By analyzing *directly* the obtained kinetics data within the framework of the first order Langmuir adsorption-desorption model we determined values of the adsorption and desorption rate constants for five different concentrations of dye solutions in 1:1 acetonitrile:tert-butanol. These values are  $k_a = 1380 \text{ M}^{-1}\text{s}^{-1}$ , and  $k_d = 3.2 \cdot 10^{-4} \text{ s}^{-1}$ . The equilibrium adsorption constant, obtained as the ratio of the latter values, is  $K_{\text{eq}} = 4.3 \cdot 10^6 \text{ M}^{-1}$ , which is in reasonably good agreement with the independent value,  $1.6 \cdot 10^6 \text{ M}^{-1}$ , determined from analysis of a measured Langmuir isotherm, considering the possible experimental errors and oversimplifying assumptions in the model. The values also agree well with several previous studies. Our experimental approach thus made it possible for the first time to extract the rate constants directly from the kinetics, which provides the values of  $k_a$  and  $k_d$  separately, and from the equilibrium Langmuir isotherm, which provides  $K_{\text{eq}}$ .

The INPS approach is thus capable of providing valuable information related to kinetics of adsorption and desorption, *and* about equilibrium adsorption.

We also compared desorption of dye molecules under different conditions (after continuous adsorption or adsorption in combination with intermittent rinsing steps and at different coverages) and for different time intervals. In agreement with earlier observations,<sup>10</sup> the desorbed amount of dye was found to be smaller when the adsorption was done in cycles, interrupted by rinsing, compared to a continuous adsorption for the same duration or to the same coverage. The fraction of desorbed molecules in a given time frame tended to be smaller for a lower dye solution concentration. However, the difference was not present when the adsorption times were 30 min or longer. These observations demonstrate deviations from first order Langmuir kinetics and show that the dye molecules in the adsorbed layer reorganize to an extent that depends on the details of the adsorption, desorption and rinsing sequences. Appropriate choice of these sequences leads to a film that is more stable toward desorption. Therefore we conclude that, despite the Langmuir kinetic approach gave reasonable results, it needs to be modified in order to account for the surface reorganization process. Furthermore we conclude that real time monitoring of the adsorption-desorption kinetics is helpful in order to optimize the properties (coverage, stability, *etc.*) of the dye adlayer.

## **Acknowledgements**

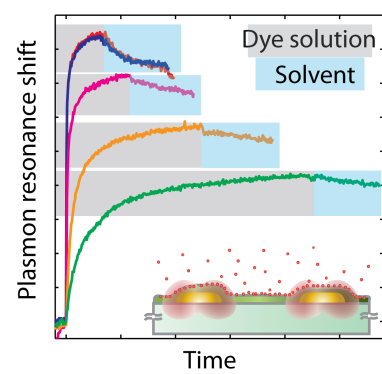


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