

***In-situ* Investigation of Dye Adsorption on TiO₂ Films Using a Quartz Crystal Microbalance with Dissipation Technique**

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Recently, dye-sensitized solar cells have achieved a record power conversion efficiency of 13.1% (0.5 sun) and 12.3% (1 sun) using a Co(II/III)tris(bipyridyl)-based redox electrolyte in conjunction with donor – π -bridge – acceptor (D- π -A) zinc porphyrin dye as sensitizer (YD2-*o*-C8) and Y123 as cosensitizer.^{1,2} We are going through a transition in the field due to recent development of new high extinction porphyrin and organic D- π -A sensitizers that are rapidly supplanting the panchromatic Ru(II) polypyridyl sensitizers. In addition, Bazzan *et al.* have shown an increase of 15% in J_{sc} and 8% in V_{oc} leading to an overall 23% increase in device performance using acetonitrile:t-butanol/H₂O adsorption/desorption cycles.³ The improvements in photocurrent and photovoltage are assumed to be due to better packing of dye molecules on the TiO₂ surface, but only indirect absorption measurements in solution or on thin transparent photoanodes could be carried out. Yet we know alarmingly little about the dynamics of dye adsorption, self-assembly of the monolayer, and formation of multilayers or aggregates. In addition, several reports have pointed out the role of molecular coadsorbates like DINHOP and Cheno that positively affect interfacial recombination and reduce aggregation.

Herein, we demonstrate for the first time the use of a liquid-phase quartz crystal microbalance with dissipation technique (QCM-D) to study dynamically and quantitatively dye sensitization of TiO₂ *in situ*.⁴ The operation principle is that of a conventional quartz crystal microbalance, measuring the shift of an electroacoustic resonance frequency upon mass loading. The measured dissipation corresponds to the damping of the oscillation and relates to the viscosity of the adsorbed layer and that of the overlying liquid, allowing for more precise interpretation of the data. We use an E4 instrument from Q-Sense, where the sensor is mounted in a temperature controlled chamber and exposed to a constant flow of solvent or dye solution on one side. Different solutions can be flowed through the chamber, starting with a reference solution that will be used as a baseline for the frequency shift, followed by sample solutions containing the species of interest. By directly measuring mass uptake, we can monitor adsorbates independently of their optical properties. Moreover, sensitivity is high enough to obtain quantitative measurements on flat surfaces enabling for the first time the investigation of the actual adsorption process, independently of the diffusion in the mesoporous film. This clear separation allows for model systems that will help understand fundamental processes in state-of-the-art DSCs.

To exemplify the concept, we have quantitatively studied dye loading for Z907, a well-studied panchromatic Ru(II) polypyridyl sensitizer and Y123, a state-of-the-art high-extinction coefficient D- π -A dye on flat TiO₂ films. We find footprints of 1.33 nm² and 0.9 nm² per molecule, respectively, which is in good agreement

with complementary fluorescence measurements. Measurements at varying concentrations and in different solvents have already yielded significant insights into the competitive adsorption between solvent and dye as well as the mechanism and kinetics of self-assembled dye monolayer formation. Furthermore, we present the first quantitative study of cosensitization with Y123 and Cheno and determine their molar ratio when coadsorbed on the surface. Finally, we demonstrate first measurements of loading of a mesoporous TiO₂ film directly attached to a QCM-D sensor, which will be important for sensing applications as well as for DSCs. Beyond QCM-D measurements on the ensemble, we will present first studies using liquid-phase AFM⁵ on the adsorbed dye monolayer, thus obtaining complementary microscopic information that may in the end lead to understanding of the adsorption mechanism on the molecular scale.

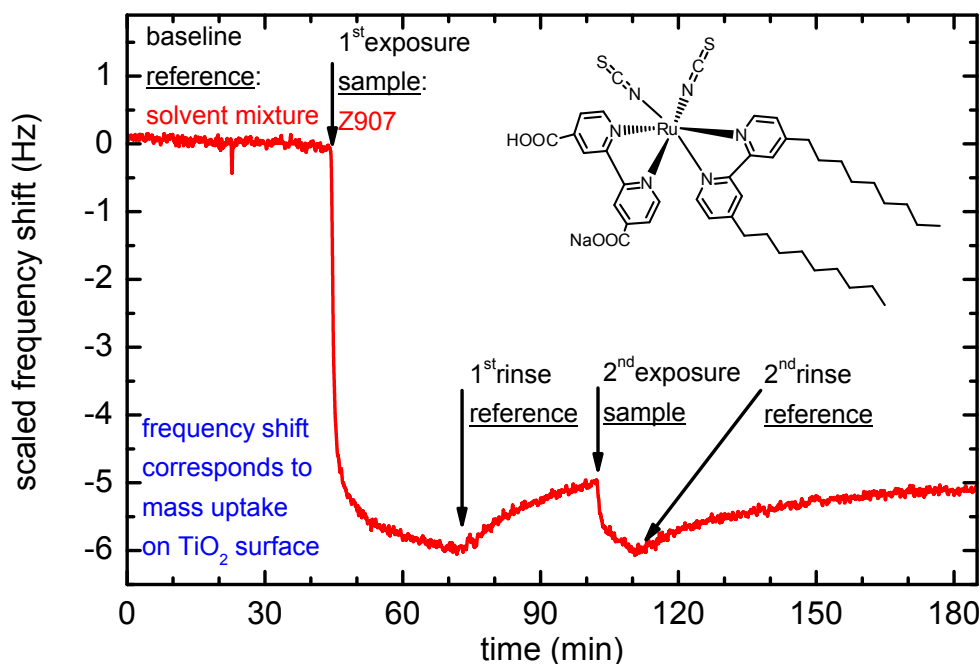


Figure 1. Frequency shift over time, showing two subsequent exposures to Z907 dye solution (55 μM in *t*-butanol:acetonitrile). The plain solvent mixture without the dye is used as a baseline and for rinsing. Here, the frequency shift corresponds directly to mass uptake.

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