IMPROVING DYE-SENSITIZED SOLAR CELLS WITH THE QCM-D TECHNOLOGY

Increased understanding and development of renewable energy sources is vital. The dye-sensitized solar cell (DSSC) is a potential alternative, or complement, to traditional solar cells. The dye molecules adsorbed on TiO_2 are critical for the light-to-electrical-energy conversion process in DSSCs. Understanding the dye adsorption mechanisms helps in optimizing the solar cells. Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D) has been used successfully to characterize these processes.

INTRODUCTION

Photovoltaic solar cells are a long term global alternative to fossil fuels for sustainable electricity generation. The dye-sensitized solar cell (DSSC) is a potential alternative, or complement, to traditional solar cells. Some of the advantages of DSSCs are that they are inexpensive to manufacture, they can be made on flexible materials and on various surfaces and they are based mainly on nontoxic materials.

A modern DSSC, the Grätzel cell, is composed of a mesoporous TiO_2 film, which is covered with a self-assembled monolayer (SAM) of dye molecules that absorb sunlight. The DSSC performance is quite dependent on how the dye is loaded into the cell. It is crucial to maximize the amount of dye but at the same time avoid multilayers. It has also been shown that molecular coadsorbates can be used to optimize the DSSC. There is an obvious need for a better understanding and optimization of the dye adsorption kinetics. Most studies, until now, have been limited to optical adsorption measurements on mesoporous substrates. A more direct method is needed to understand the mechanisms of adsorption of the dye.

QCM-D offers an in situ liquid-phase analytical technique to quantify the amount, saturation time and adsorption kinetics of dye uptake on flat and mesoporous TiO_2 films. The QCM-D technology is independent of the optical properties of the adsorbate, which means that also coadsorbates with no optical signature can be quantified. As a result of the high sensitivity, quantitative measurements can also be performed on flat surfaces enabling detailed investigation of the adsorption process, independently of the diffusion in the mesoporous film, which helps understanding the fundamental processes in the DSSCs.

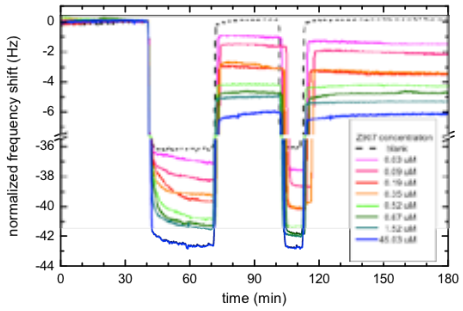

Figure 1. Frequency shift upon exposure to dye at different concentrations on a flat TiO_2 surface. Shown are two subsequent exposures to dye with a rinse after each. The frequency shift is represented by the 7th overtone (normalized) and is generally related to mass changes occuring on the surface.

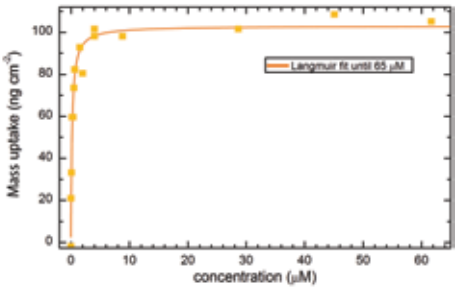

Figure 2. Final mass uptake as a function of dye concentration and the fitted Langmuir adsorption isotherm (orange curve). Adsorption took place on a flat TiO_2 surface. Data used was from measurements at the 7th overtone.

EXPERIMENTAL

The adsorption of dye was measured with the QCM-D technology, first using sensors with a flat TiO_2 surface followed by sensors with a mesoporous TiO_2 surface. Studying the adsorption processes on a flat surface provides insight into the different adsorption mechanisms, independent of transport effects due to surface porosity. However, the mesoporous surface is used in the real case, the solar cell, so this is more realistic and interesting in that sense. The QCM-D technology is a useful tool for both kinds of studies.

RESULTS AND DISCUSSION

The adsorption of dye molecules was first studied on a flat TiO_2 surface and the effect of concentration was investigated. Figure 1 shows how the amount of adsorbed dye varied with varying dye concentration in the solution.

By adding a negative control with solvent only, the influence of the bulk liquid effects could be measured and subtracted. Since the adsorbed layer was shown to be rigid (no dissipation shift, data not shown), the frequency shift is directly proportional to the mass adsorbed. A second exposure to the dye did not result in a significant mass uptake, indicating that close to equilibrium has been reached.

By using the data in Figure 1, the total mass uptake after rinse was plotted as a function of concentration of dye solution. Data points were fitted with a Langmuir isotherm to extract the equilibrium adsorption constant (Figure 2). From the saturation value for the mass uptake, which corresponds to full monolayer coverage, the projected area per molecule was calculated.

By performing QCM-D adsorption measurements with dye and dye + coadsorbate and combining the results with fluorescence measurements of the molecules desorbed from the surface, the molar ratio when both molecules are coadsorbed could be calculated. After characterizing the adsorption onto a flat TiO_2 surface, the same event was studied using a mesoporous surface. Figure 3 shows the frequency shift as the dye was adsorbed onto a 2 µm thick mesoporous TiO_2 film. The concentration of the dye was 250 µM.

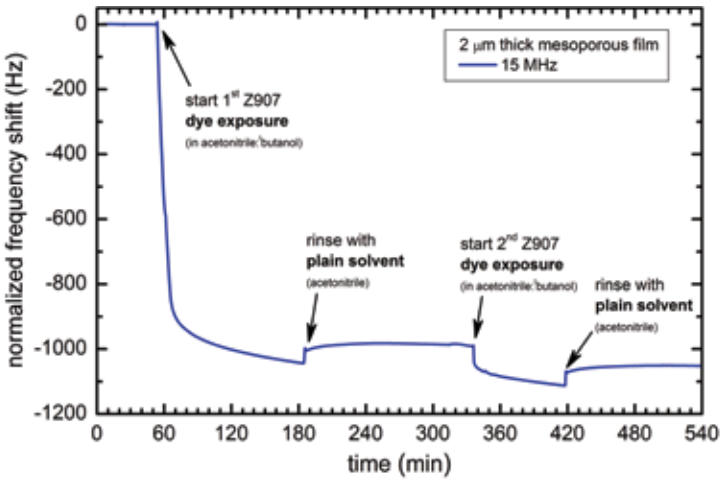

Figure 3. Frequency shift as dye, at a concentration of 250 µM, was added to a mesoporous surface. Shown are two subsequent exposures to dye with a rinse after each. The frequency shift is represented by the 3rd overtone (normalized) and is generally related to mass changes occuring on the surface.

The frequency shift was increased by two orders of magnitude as compared to dye adsorbed to a flat surface (i.e. 5.5 Hz for 250 µM). This difference demonstrates the much larger mass uptake on mesoporous TiO_2 than on flat TiO_2.

CONCLUSIONS

The QCM-D technology was successfully used to quantify the amount, saturation time and kinetics of dye uptake on flat and mesoporous TiO_2 films. By characterizing these adsorption processes, better dye-sensitized solar cells can be developed and thereby contribute to a more sustainable energy situation worldwide.

ACKNOWLEDGEMENTS

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REFERENCES

Hauke A. Harms, Nicolas Tétreault, Viktoria Gusak, Bengt Kasemo and Michael Grätzel. *In situ investigation of dye adsorption on TiO_2 films using a quartz crystal microbalance with a dissipation technique.* Phys. Chem. Chem. Phys., 2012,14, 9037-9040.

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