

Vesicle adsorption on Titanium Oxide investigated by simultaneous QCM-D and NPS measurements

The combination of two label-free, surface sensitive measurement techniques based on different physical principles- Insplorion's NanoPlasmonic Sensing (NPS) and Q-Sense quartz crystal microbalance with dissipation monitoring (QCM-D) enables detailed studies of biomacromolecular interactions at solid-liquid interfaces.

In this application note, the two complementary techniques are used to study the details of vesicle adsorption without rupture.

Introduction

Vesicle adsorption and rupture leading to supported lipid bilayers (SLBs) is a classic example of molecular self-assembly. The well understood process of SLB formation is governed by various factors such as vesicle properties (size), and surface chemistry and has been highly scrutinized.

The details of vesicle adsorption without rupture are less thoroughly understood. One reason for this is that it is difficult to separate signal responses arising from the total number of adsorbed vesicles vs. vesicle deformation using a single measurement technique.

NPS and QCM-D are complementary techniques since both the measured quantities ("dry" (optical) vs. "wet" (acoustic) mass) and the probe depths of the two techniques (a few hundred nm for QCM-D and ~30 nm for NPS) are different.

By studying the simultaneous QCM-D and NPS responses it is possible to scrutinize the adsorption process of intact vesicles.

Experimental Procedure

The experiments were performed using TiO₂ coated Acoulyte sensors. The sensors were cleaned in a solution of 1% SDS, rinsed with

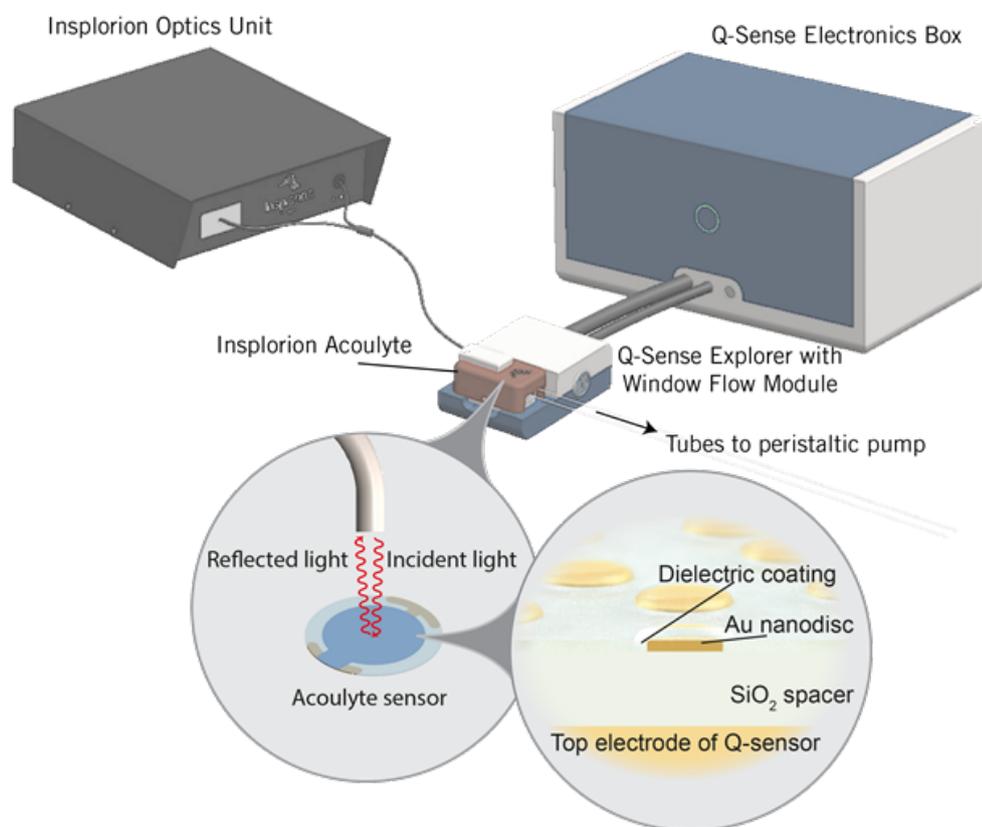


Figure 1: The Insplorion Acoulyte module is mounted on a Q-Sense E1/Explorer instrument and the Acoulyte sensor is used in the flow cell.

water and ethanol, blow-dried in N₂ and cleaned using an oxygen plasma cleaner before being mounted in the flow module. DOPC vesicles of varying diameters diluted in Tris-buffer solution were flown over the Acoulyte sensor and the resulting QCM-D frequency and NPS wavelength shifts were monitored. A schematic of the experimental setup is shown in Figure 1.

Results and Conclusion

The adsorption process was investigated with an emphasis on vesicle size. The QCM-D and NPS measurement signals reveal different trends with increasing vesicle size (bar graph in Figure 2). The final saturation values of the NPS signal is highest for the intermediate sized vesicles indicative of a larger amount of (dry) vesicle mass

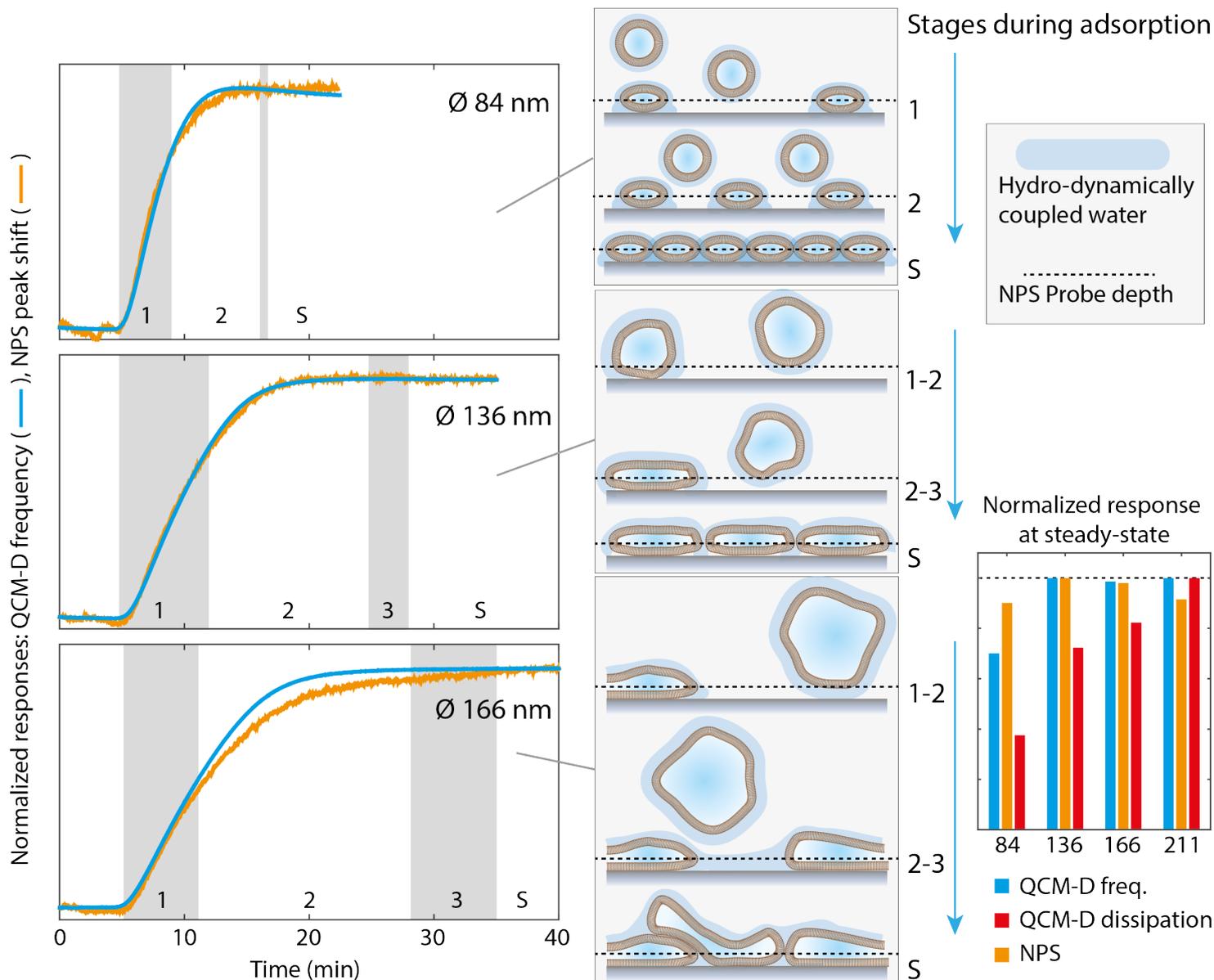


Figure 2: QCM-D (blue) and NPS (orange) data for the adsorption of DOPC vesicles on a TiO_2 surface. Each graph shows data from vesicles of different diameters. The simplified schematics show the general vesicle adsorption behaviour for each size of vesicles. Data from reference [1].

in close proximity to the surface for these vesicles. This is due to the effect of size on packing coverage and deformation of the adsorbed vesicles. By studying the adsorption kinetics for the differently sized vesicles (shown in the graphs in Figure 2) more detailed information on the process can be found. The longer time to reach equilibrium seen for both QCM-D and NPS signals as vesicle

size increase is expected due to diffusion-limited adsorption. In all cases there is an initial linear phase followed by a decline in response increase. The deviation between the QCM-D and NPS signals especially evident for the larger vesicles is indicative of an increased importance of coupled solvent and steric effects. By comparing the NPS and QCM-D signals it is possible to define a

number of stages during the adsorption process schematically outlined for each vesicle size in Figure 2.

The different trends in saturation signals and kinetics shown here underscore the benefits of combining multiple measurement techniques to reveal new information.

This study was performed by Prof. Nam-Joon Cho and coworkers at Nanyang Technological University. The results were first published in [1].

Reference

[1] A.R. Ferhan, J.A. Jackman, and N.Cho, Phys. Chem. Chem. Phys., 2016, DOI: 10.1039/C6CP07930J