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Experimental investigation of the thickness, hydrogen bonding states, and viscoelasticity of interfacial water on solid surfaces

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Doctor of Science
Graduate major in Human-Centered Science and Biomedical Engineering

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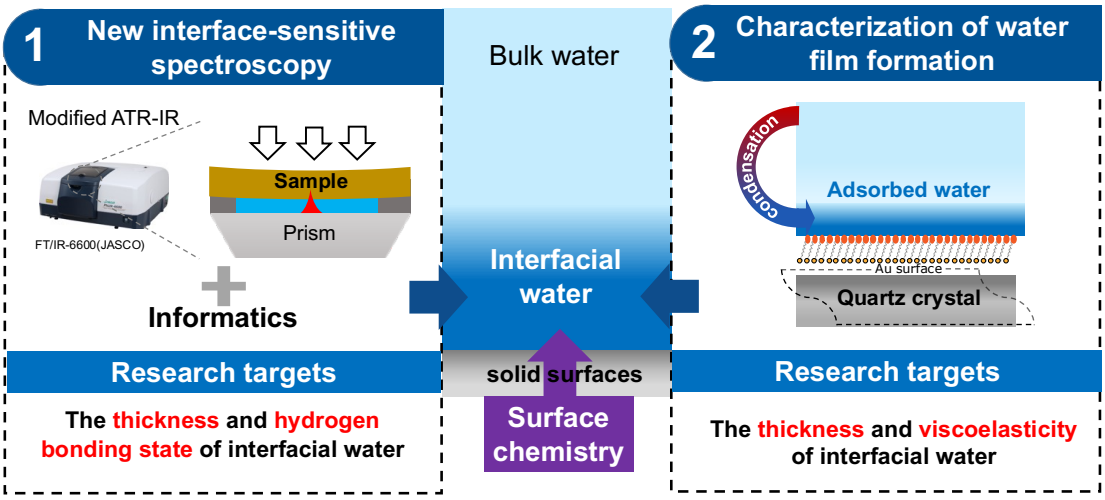
Thesis Outline



Chapter I: Introduction

The water/solid interfaces are ubiquitous in nature and play significant roles in chemistry, biology, tribology, and industry.[1–4] Macroscopic wettability/surface tension measurements (i.e., water contact angle) are often used to assess the affinity between water and solid surfaces. However, it has been revealed that such macroscopic wettability is not always a good indicator of interfacial phenomena, such as protein adsorption, wetting process, etc. A microscopic understanding of the behavior of water near solid surfaces is highly desired.

During the past decades, many surface-sensitive techniques have been developed to study interfacial water near solid surfaces. Interfacial regions within several nanometers have been discovered on various hydrophilic/hydrophobic surfaces using X-ray reflectometry and frequency-modulated atomic force microscopy, where water has a different density profile compared to bulk water. Nevertheless, the behaviors of water in the interfacial region have yet to be fully understood

due to the experimental difficulty. For example, conventional surface-sensitive vibrational techniques are difficult to assess the entire interfacial region because of the limitation in detecting range and the challenge of quantitative analysis. Additionally, normal microscopic imaging techniques are incapable of probing the evolution of the interfacial water on the nanoscale due to the limitation in temporal/spatial resolution.

Chapter II: Principles and Theoretical Aspects of the techniques used in this thesis work

This doctoral thesis is focused on developing new analytical approaches to investigate the entire interfacial region. The principles and theoretical aspects of the techniques used in this thesis work are briefly described. The first method was a new surface-sensitive vibrational spectroscopy based on a combination of linear spectroscopy and informatics. This method enables the characterization of the thickness and hydrogen bonding state of water in the entire region. The second method was a real-time characterization of water film formation by employing the quartz crystal microbalance with energy dissipation monitoring (QCM-D). The method allows the investigation of the evolution of the water-surface interaction, and the viscoelasticity of the growing water film.

Chapter III: Evaluation of the hydrogen bonding state and thickness of interfacial water using a new interface-sensitive analytical method based on a combination of linear spectroscopy and informatics

The capability of the developed surface-sensitive vibrational spectroscopy to characterize the thickness and molecular vibrations of interfacial water was first demonstrated using well-defined hydrophobic and hydrophilic surfaces. The results validated previous findings obtained by surface-sensitive techniques and further complemented the prior observations from the perspective of the entire interface region. Furthermore, this method was utilized to investigate the impact of surface chemistry on interfacial water. It was found that the physicochemical properties of the surface can dictate the thickness and hydrogen bonding state of the interfacial water, even though the surfaces have similar macroscopic wettability.

Chapter IV: Evaluation of water film formations on model surfaces by quartz crystal microbalance with energy dissipation monitoring (QCM-D)

Self-assembled monolayers (SAMs) were employed to construct the surfaces with different chemical properties, including hydrophobic (CH_3 and CF_3), hydrophilic protein-adsorbing (OH), and hydrophilic protein-resistant [sulfobetaine, SB, and oligo(ethylene glycol), EG3-OH] terminated SAMs. It was found that the kinetics of the water condensation exhibit critical dependence on the physicochemical properties of the surface. By comparing the viscoelasticity measurements from the QCM-D, I discovered that the strengths of the water-SAM interactions deviate from expectations based on the macroscopic water contact angles but were shown to be consistent with predictions of molecular simulations instead. In addition, I also observed the presence of a stiffer interfacial water layer in the range of 2-3 nm on protein-resistant SAMs, while the thicknesses of the interfacial water on either hydrophilic protein-adsorbing OH SAM or hydrophobic SAMs exhibited small (< 1 nm). By combining our observations and results from the literature, I concluded that the strength of water-SAM interaction is a primary factor in modulating the viscoelasticity of the interfacial water layer, and the range of modulation also depends on the terminal groups.

Chapter V: Summary and Conclusions

Two new strategies were successfully devised to investigate the behavior of water in the entire interfacial region. The major advantage of the present methods is that they can provide information on the thickness and physicochemical properties of interfacial water, which is challenging with traditional analytical techniques. It was revealed that the physicochemical properties of the surface modulate the hydrogen bonding state and viscoelasticity of interfacial water, and the modulation extends to different thicknesses depending on the water-surface interaction. The results also showed that the interfacial behavior of water does not necessarily correlate with macroscopic water angles, indicating the necessity of studying interfacial water to fully understand the interfacial phenomena. The methods can be widely used to study the behavior of interfacial water near various materials (i.e., polymer, metal, oxide, lipid bilayer) and provide quantitative bases for designing novel water/solid interfaces.

Major References

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