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著者(和文)	SongSubin
Author(English)	Subin Song
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種別(和文)	論文要旨
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（博士課程）
Doctoral Program

論 文 要 旨

THESIS SUMMARY

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学生氏名： Student's Name	Song subin		指導教員（主）： Academic Supervisor(main)	Tomohiro HAYASHI
			指導教員（副）： Academic Supervisor(sub)	

要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

Water is present on most solid surfaces and plays significant roles in chemistry, biology, tribology, industry, etc. 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 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.

Recently, 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 been 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.

This doctoral thesis is focused on developing new analytical approaches to investigate the entire interfacial region. 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.

The main strategy of the first method is to modulate the signal ratio between interfacial and bulk water by controlling the distance between the sample and prism, and then apply the informatics to separate the two signals. Moreover, the thickness of interfacial water can be calculated based on the obtained concentration profiles of the two components. This method 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 water contact angles. These findings may explain the mechanism underlying interfacial phenomena where interfacial water is involved, such as controlled drug release, antifouling processes, etc.

To investigate the evolution of interfacial water, I equipped the QCM-D with a precise dew point generator to allow the real-time characterization of the initial water condensation process. 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.

Altogether, I successfully devised two new strategies 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.