

Exotic Structures, Physicochemical Properties and Quantum Dynamics of Interfacial Water

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Keywords Surface & Interface Science, Nonlinear Optical Spectroscopy, Water Molecules

Interfacial water is ubiquitous in nature and plays crucial roles in a variety of disciplines, including physics, chemistry and biology. In such a symmetry-breaking system, not only adsorption geometry but also anisotropic molecular orientation (H-up/H-down configuration) is a key structural parameter that determines unique physicochemical properties of interfacial water systems. Nevertheless, orientation of water molecules, *i.e.* configuration of hydrogens, in the interfacial hydrogen-bond network is extremely hard to investigate with traditional experimental techniques such as electron diffraction, grazing X-ray scattering and even scanning probe microscopy, because hydrogen has only a single electron and responds extremely weakly to the probes of these techniques. Therefore, the determination of molecular orientation of interfacial water has been an experimental challenge.

We have used heterodyne-detected sum-frequency generation spectroscopy for unveiling molecular orientation of interfacial water system. The remarkable feature of this technique is that $\text{Im}\chi^{(2)}$ SFG spectra ($\chi^{(2)}$: The second-order nonlinear

susceptibility) obtained by the heterodyne detection exhibit positive or negative sign for net orientation of OH with hydrogen pointing away (H-up) or toward substrate (H-down), respectively. Thus, the heterodyne-detected $\text{Im}\chi^{(2)}$ SFG has a great advantage to direct observation of water orientation that cannot be investigated through other traditional experimental methods. With this sophisticated molecular spectroscopy technique, we have conducted a series of pioneering research on unique structures and physicochemical properties of hydrogen bonds of interfacial water molecules.

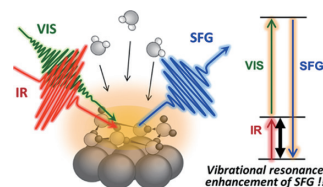


Figure 1. Infrared-visible sum-frequency-generation (SFG) spectroscopy of water molecules on solid surface.

Selected Publications

- T. Sugimoto *et al.*, “Topologically Disordered Mesophase at Top-most Surface of Crystalline Ice Between 120 and 200 K,” *Phys. Rev. B* **99**, 121402(R) (2019).
- F. Kato *et al.*, “Direct Experimental Evidence for Markedly Enhanced Surface Proton Activity Inherent to Water Ice,” *J. Phys. Chem. Lett.* **11**, 2524–2529 (2020).
- T. Sugimoto *et al.*, “Orientational Ordering in Heteroepitaxial Water Ice on Metal Surfaces,” *Phys. Chem. Chem. Phys.* **29**, 16435–17012 (2020).
- H. Sato *et al.*, “Critical Impacts of Interfacial Water on C–H Activation in Photocatalytic Methane Conversion,” *Commun. Chem.* **6**, 8 (2023).
- H. Sato *et al.*, “Beyond Reduction Cocatalysts: Critical Role of Metal Cocatalysts in Photocatalytic Oxidation of Methane with Water,” *Angew. Chem., Int. Ed.* **62**, e2023060 (2023).
- S. Takahashi *et al.*, “Broadband Tip-Enhanced Nonlinear Optical Response in a Plasmonic Nanocavity,” *J. Phys. Chem. Lett.* **14**, 6919–6926 (2023).

1. Positive and Negative Impacts of Interfacial Hydrogen Bonds on Photocatalytic Hydrogen Evolution¹⁾

Hydrogen production via photocatalytic water splitting is a sustainable solution for next-generation energy by utilizing light energy at room temperature. However, the design of innovative photocatalysts remains a challenge due to a limited molecular-level understanding of interfacial water molecules and their hydrogen bond networks. Unveiling the physico-chemical properties of these interfacial water molecules is critical to optimizing photocatalytic efficiency and achieving breakthroughs in sustainable hydrogen production.²⁾

We have comprehensively investigated the impact of interfacial H-bond networks using various TiO₂ photocatalysts and uncovered a crucial role of interfacial H-bond structure/dynamics and optimal interfacial water environment for H₂ evolution. We controlled the thickness of adsorbed water from sub-monolayer to multilayers by precisely adjusting water vapor pressure. With this approach, we succeeded in directly demonstrating the correlation between H₂ formation rate and the microscopic structure of H-bond networks using real-time mass spectrometry and infrared absorption spectroscopy. Regardless of the crystalline structure of the TiO₂ photocatalyst, we observed a linear increase in H₂ formation rate with water adsorption up to three layers, indicating that reactive water molecules are present not only in the first adsorbed layer but also in several overlying layers (Figure 1). However, the H₂ formation rate turned to decrease dramatically when more than three layers of water covered the TiO₂ surface (Figure 1). In this situation, infrared spectra clearly indicated two distinct types of adsorbed water on the TiO₂ surface: Interfacial water and liquid-like water. Due to many-body interactions among adsorbed water molecules, the liquid-like water adsorbed in more than three layers led to strengthening of interfacial H-bond, which hinder interfacial proton-coupled hole transfer and drastically decreased the H₂ formation rate. Based on these microscopic insights, their study suggests that depositing three water layers in a water vapor environment is optimal for photocatalytic hydrogen evolution. These findings open new avenues for the molecular-level design and engineering of interfacial water toward the development of more innovative photocatalytic systems for next-generation renewable energy production.

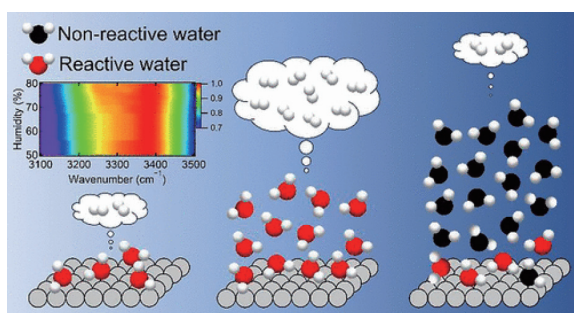


Figure 2. Identifying the reaction conditions that maximize catalytic activity in photocatalytic hydrogen evolution under water vapor atmospheres.

2. Direct Operando Identification of Reactive Electron Species Driving Photocatalytic Hydrogen Evolution on Metal-Loaded Oxides³⁾

Understanding of reactive electron species and active reaction sites on photocatalytic reduction reaction are vital for designing and manufacturing innovative catalysts with improved evolution activity of hydrogen as sustainable energy carrier.

We succeeded in significantly suppressing the signals derived from thermally excited electrons and observing the reactive photogenerated electrons contributing to the photocatalytic hydrogen evolution. Such innovation was achieved by a new method based on synchronization of the millisecond periodic excitations of photocatalysts with a Michelson interferometer used for FT-IR spectroscopy.⁴⁾ This demonstration was achieved for metal-loaded oxide photocatalysts under steam methane reforming and water splitting conditions. Although it has long been conventionally believed that loaded metal cocatalysts function as sinks for reactive photogenerated electrons and active sites for reduction reactions, we found that the free electron species in the metal cocatalysts were not directly involved in the photocatalytic reduction reaction. Alternatively, the electrons shallowly trapped in the in-gap states of oxides contributed to enhancing the hydrogen evolution rate upon the loading of metal cocatalysts. The electron abundance in the in-gap states, especially metal-induced semiconductor surface states, was clearly correlated to the reaction activity, suggesting that such metal-induced semiconductor surface states formed in the periphery of the metal cocatalyst play key roles in the photocatalytic hydrogen evolution. These microscopic insights shift a paradigm on the traditionally believed role of metal cocatalysts in photocatalysis and provide a fundamental basis for rational design of the metal/oxide complex interfaces.

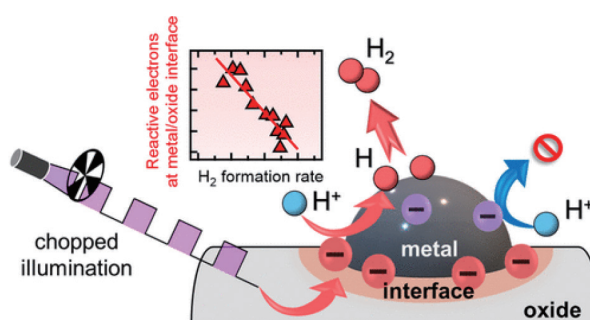


Figure 3. Unveiling actual role of metal cocatalysts. Electrons in cocatalyst periphery drive photocatalytic hydrogen evolution.

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