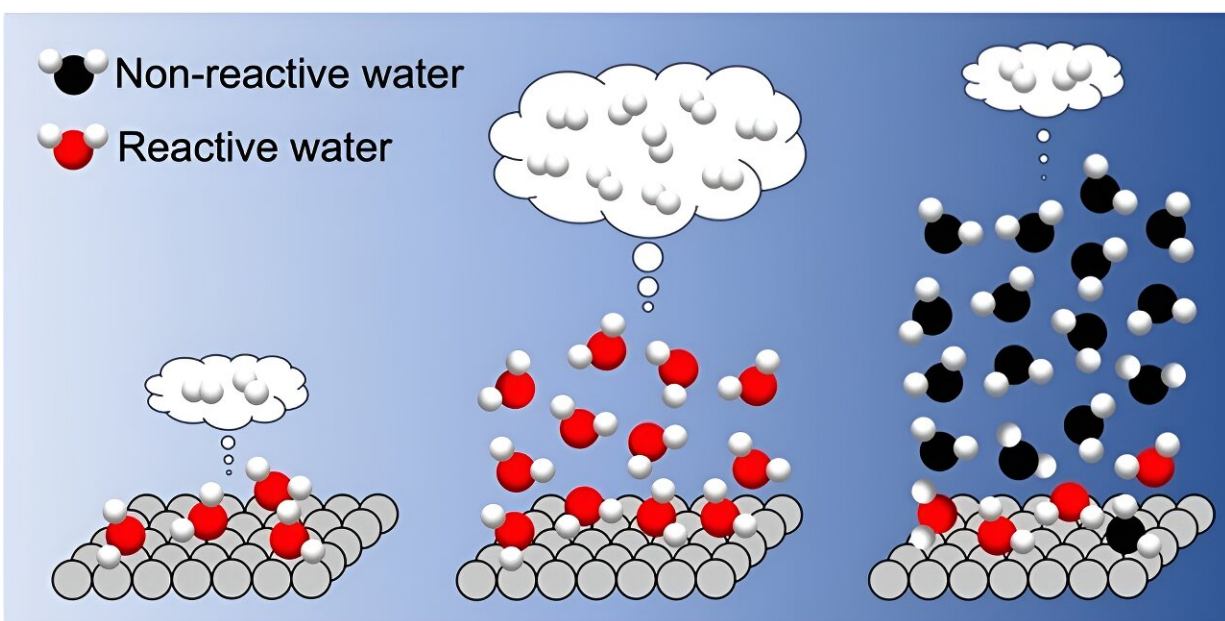


New insights into interfacial hydrogen bonds could enhance photocatalytic hydrogen evolution

July 19 2024



Schematic of changes in the reaction activity associated with variation of water layer thickness on the photocatalyst surface. The H_2 formation rate increases with increasing water layers up to three layers. When more than three water layers cover the surface, the liquid-like water overlayers strengthen/harden the interfacial H-bond networks. The hardened interfacial H-bond networks hinder the interfacial proton-coupled hole transfer, resulting in a dramatic decrease in the H_2 formation rate. Credit: Zhongqiu LIN, Toshiki Sugimoto

Photocatalytic hydrogen evolution from water is a key technology for achieving sustainable hydrogen production. However, the direct impact of the microscopic structure of interfacial water molecules on photocatalytic reactivity remains unexplored.

In a study, [appearing](#) in *Journal of the American Chemical Society*, the crucial roles of interfacial hydrogen bond structure and dynamics, as well as the optimal interfacial water environment for promoting H₂ evolution were uncovered. The paper is titled "Positive and negative impacts of interfacial hydrogen bonds on [photocatalytic](#) hydrogen evolution."

These findings provide molecular-level insights that can guide the design of interfacial water conditions to enhance photocatalytic performance.

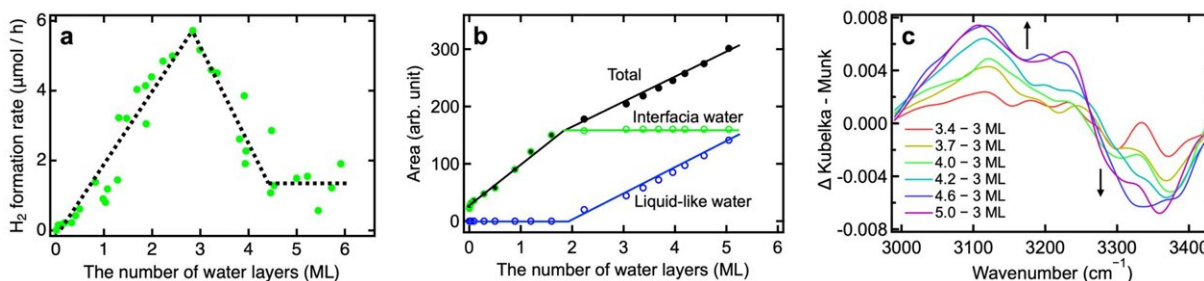
Hydrogen production via photocatalytic water splitting is a sustainable solution for next-generation energy by utilizing [light energy](#) at room temperature. However, the design of innovative photocatalysts remains a challenge due to a limited molecular-level understanding of interfacial water molecules and their hydrogen bond networks.

Unveiling the physicochemical properties of these interfacial water molecules is critical to optimizing photocatalytic efficiency and achieving breakthroughs in sustainable hydrogen production.

Researchers (Zhongqiu Lin and others) led by Toshiki Sugimoto, Associate Professor at Institute for Molecular Science / The Graduate University for Advanced Studies, SOKENDAI, 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.

They controlled the thickness of adsorbed water from sub-monolayer to multilayers by precisely adjusting water vapor pressure. With this approach, they 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 (brookite, anatase, or a mixture of anatase and rutile), they 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.



(a) Change in the rate of hydrogen formation through photocatalytic water splitting when the number of water layers (amount of adsorbed water molecules) is systematically changed under various water vapor pressures. (b) The dependency of the O–H stretching band area on the number of water layers (black: total spectrum area, green: spectrum area of interfacial water component, blue: spectrum area of liquid-like water component). The spectrum of the interfacial water component, which shows a spectral shape clearly different from that of bulk liquid water, is nearly saturated in area at two molecular layers, while the liquid-like water component, which shows a spectral shape almost the same as that of bulk liquid water, increases when water molecules are adsorbed in layers thicker than three. (c) Change in the O-H vibration spectrum of the interfacial water component induced by the adsorption of more than three molecular layers of water. Credit: Zhongqiu LIN, Toshiki Sugimoto

However, the H₂ formation rate turned to decrease dramatically when more than three layers of water covered the TiO₂ surface.

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 the interfacial H-bond, which hindered 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.

Photocatalysis has been extensively studied for over half a century, predominantly in aqueous solution environments. In this context, this study represents a potential paradigm shift, demonstrating the effectiveness of water vapor environments compared to traditional liquid-phase reaction systems.

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.

More information: Zhongqiu Lin et al, Positive and negative impacts of interfacial hydrogen bonds on photocatalytic hydrogen evolution, *Journal of the American Chemical Society* (2024). [DOI: 10.1021/jacs.4c04271](#)

Provided by National Institutes of Natural Sciences

Citation: New insights into interfacial hydrogen bonds could enhance photocatalytic hydrogen evolution (2024, July 19) retrieved 19 July 2024 from <https://phys.org/news/2024-07-insights-interfacial-hydrogen-bonds-photocatalytic.html>

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