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Water adsorption induced photogenerated carrier dynamics at the surface of anatase TiO₂ nanoparticles under water vapor environment

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Heterogeneous photocatalytic water splitting with semiconductor-based materials is composed of a couple of major processes: generation of electrons and holes by optical transitions, charge separation and trapping, and redox reactions of water at the surface of photocatalyst. Because charge recombination results in a direct loss of redox ability of photocatalysts, the charge separation and the following charge carrier trapping play a vital role at an early stage of photocatalysis and dominate the efficiency of water splitting [1,2]. Although hole trapping by water at water/photocatalyst interface is the first step of oxygen evolution in the water splitting, little has been known on how water adsorbate itself is involved in hole trapping dynamics.

To clarify this point, we have constructed a water-vapor-pressure controllable high-vacuum chamber and investigated the effect of water adsorption on charge dynamics in nanoparticles of anatase TiO₂ nanoparticles by measuring transient IR absorption time profiles and steady-state spectra as a function of the number of adsorbed water layer [3]. Through the analysis of adsorption-state selective adsorption isotherms, we found that water molecules in the first layer strongly interacting with TiO₂ surface are capable to effectively trap photogenerated holes at the surface. Interestingly, the adsorption of second-layer water weakens the interaction between first layer water and TiO₂ surface, which results in the loss of the hole trapping capability of water in the first layer. These findings clearly indicate that not only the inherent property of photocatalyst itself, but also water adsorption and hydrogen bonding among the water molecules surrounding catalysts are important factors for the dynamics of photogenerated charges and, hence, its photocatalytic activity [3].

[1] N. Aiga, Q. Jia, K. Watanabe, A. Kudo, T. Sugimoto & Y. Matsumoto, *J. Phys. Chem. C* 117, 9881 (2013).

[2] M. Yabuta, T. Takayama, K. Shirai, K. Watanabe, A. Kudo, T. Sugimoto & Y. Matsumoto, *J. Phys. Chem. C* 118, 10972 (2014).

[3] K. Shirai, T. Sugimoto, K. Watanabe, M. Haruta, H. Kurata & Y. Matsumoto, *Nano Lett.* 16, 1323 (2016).

