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 (Fig. 1). Because charge recombination results in a direct loss of redox ability of photocatalysts, the charge separation and trapping are key processes at an early stage of photocatalysis [1].

We have constructed a gas-pressure controllable high-vacuum chamber and conducted femtosecond pomp-probe spectroscopy and steady-state diffuse-reflectance Fourier-transform infrared (DRFTIR) spectroscopy for anatase-TiO$_2$ nanoparticles (ST-01 purchased from Ishihara sangyo: typical particle size is ~5 nm, Fig. 2) under water-vapor atmosphere in the pressure range from $10^{-4}$ to $10^3$ Pa. Transient absorption (TA) at a probe-light wavelength of 500 nm after the excitation of in-gap states with 400 nm pump light showed a fast decay of holes within ~5 ps; the decay characteristics are independent of water-vapor pressure. In contrast, TA at 4000 nm (2500 cm$^{-1}$) after irradiation of 400 nm pump light showed a fast decay within ~5 ps followed by a slow decay with a decay constant longer than 100 ps. In the case of TiO$_2$, TA of infrared light is due to free electrons in the conduction band and electrons localized in shallow trap sites [2,3]. Thus, the origin of the slow decay component of TA is trapped electrons. The intensity of this component significantly depended on the water-vapor pressure as shown in Figure 3(a). Also shown in the figure is the relative coverage of first-layer water molecules directly adsorbing on bare TiO$_2$ surfaces or surface hydroxyl groups without second-layer water adsorbate, which was derived from the analysis of DRFTIR spectra for OH stretching bands. A good correlation between the two curves in Figure 3(a) indicates

Figure 1. Schematic illustration of heterogeneous photocatalytic water splitting.

Figure 2. TEM image of TiO$_2$ nanoparticles (ST-01).
that the first-layer water molecules create electron trap sites, while the following second-layer water adsorption annihilates them.

To clarify the adsorbed state of water molecules that significantly affect the electron trapping, we have developed an analytical method that directly transforms adsorption isotherm, i.e. DRFTIR intensity as a function of water-vapor pressure, into the adsorption density of states (ADOS, \(g(E)\)) of nanoparticle surfaces on the basis of the Langmuir-type adsorption-desorption rate equation (2), taking into account the distribution of adsorption energy (\(E\)) on inhomogeneous surfaces as follows:

\[
\text{Adsorption isotherm} \quad \sigma_{eq}(p) = \int_{-\infty}^{0} g(E)\theta_{eq}(E; p)\,dE \ldots (1)
\]

\[
\frac{d\theta(E; t)}{dt} = k_a(E)n(t)[1 - \theta(E; t)] - k_d(E)\theta(E; t) \ldots (2)
\]

where \(p\) is the pressure of water vapor, \(\mu_g\) the chemical potential of three dimensional translation of water molecule, \(n\) the number density of water molecules in the gas phase, \(k_B\) the Boltzman constant, \(T\) the temperature, \(k_a\) and \(k_d\) are rate constants of adsorption and desorption, respectively. At adsorption-desorption equilibrium condition, occupancy of a single adsorbed state \(\theta_{eq}(E; p)\) is well approximated as the Fermi–Dirac distribution function [4]. Sommerfeld expansion of the right side of eq. (1) revealed that the ADOS of first-layer water molecules that create the electron trap sites are distributed from -0.9 to -0.6 eV, while that of second-layer water molecules that annihilate trap sites are distributed from -0.6 to -0.5 eV (Fig. 3(b)).

![Figure 3](image)

**Figure 3.** (a) The intensity of TA and DRFTIR spectra as a function of water-vapor pressure, (b) adsorption density state derived from the intensity of DRFTIR and eq. (1).