Understanding Charge-Transfer Reactions by Constrained Density Functional Theory

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To solve energy problems, photocatalysts have been actively studied for, e.g., decomposing water into hydrogen and oxygen using sunlight. Developing high-performance photocatalysts requires the molecular-level understanding of charge-transfer reactions in photocatalytic processes. However, even for TiO_2, the mechanism shown in Figure 1 remains unclear. This is partly because photocatalysis involves complex charge-transfer reactions

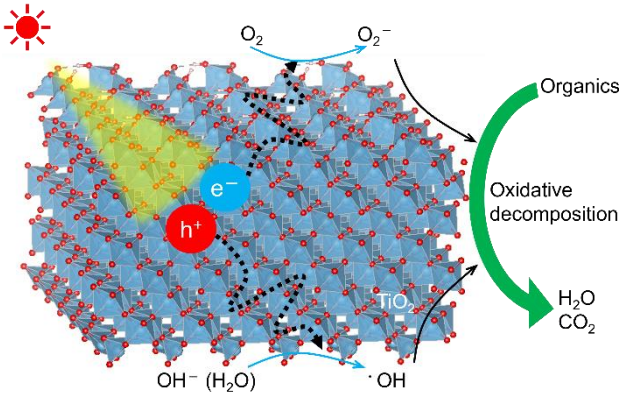

Figure 1. Schematic of charge-transfer reactions in TiO_2 photocatalysis

The aim of this presentation is to understand the charge-transfer reactions in condensed phases *e.g.* TiO_2 photocatalysts by using density functional theory (DFT) calculations. Here, the constrained DFT (CDFT) method is employed to simulate the localized charges. First, we validate the method by molecular dynamics simulations of proton transfer in aqueous silicic acid.[1,2] In this study, we propose a computational scheme for proton transfer using *ab initio* molecular dynamics (MD) simulations and CDFT. We also plan to talk about another application in aqueous solutions. Next, the facet (directional) dependence by polaron migration is clarified in anatase TiO_2 and compared with the experiment.[3] We focus on the discussion of hole migration in bulk anatase TiO_2 and at its surfaces.

In this study, DFT calculations were carried out under three-dimensional periodic boundary conditions using the cp2k program package. For the proton transfer in aqueous solutions, the proposed CDFT method employs the vertical energy-gap coordinate defined by the difference of energies for the reactant and product states, which are defined by different charge constraints to the O atom of proton donor with the Becke density partitioning method. For the polaron transfer in anatase TiO_2, five anatase surfaces were used to study the facet dependence of the stability of surface-trapped holes. To achieve hole formation, the CDFT method was used to optimize all ion coordinates while varying the number of valence electrons on a single O atom.

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Figure 2 shows the calculated free energy surface in aqueous silicic acid, and the reaction free energy of deprotonation agrees with the experimental results within a few kcal/mol. There are three main features of the CDFT method: 1. it can be applied not only to homogeneous systems but also to heterogeneous systems; 2. the reaction coordinate is straightforwardly defined; 3. it is easy to perform dynamical analysis[4] such as transmission coefficients.

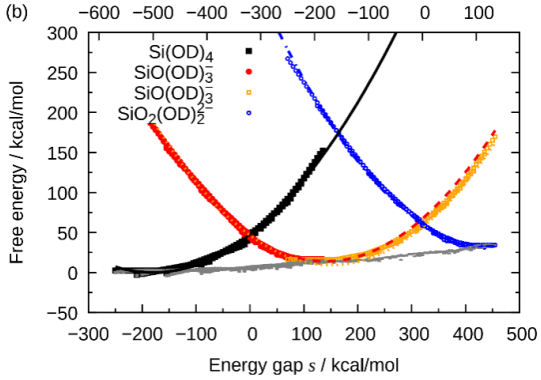

Figure 2. Computed free-energy surfaces of the deprotonation reaction of aqueous orthosilicic acid. The gray points are the adiabatic free-energy surface (FES).

Figure 3 shows (a) the potential energy profile of holes (hole trapping energy) and (b) the spin density on an anatase TiO_2 surface with five facets. The profiles are strongly dependent on the crystal facet. For the hydroxylated (112) and (001) surfaces, the holes are most stable on the O atoms of the OH groups on the surface. This is consistent with the best photocatalytic performance on the (112) surface measured experimentally, which is one order of magnitude greater than the well-known Degussa P25 commercially available. It is also found that the hole transfer along the [112] direction in anatase TiO_2 is fastest among all directions, which also supports the experimental findings. These results indicate that, although the (101) surface is the most thermodynamically stable, the (112) and (001) surfaces provide higher active sites for photocatalytic degradation of organic molecules.

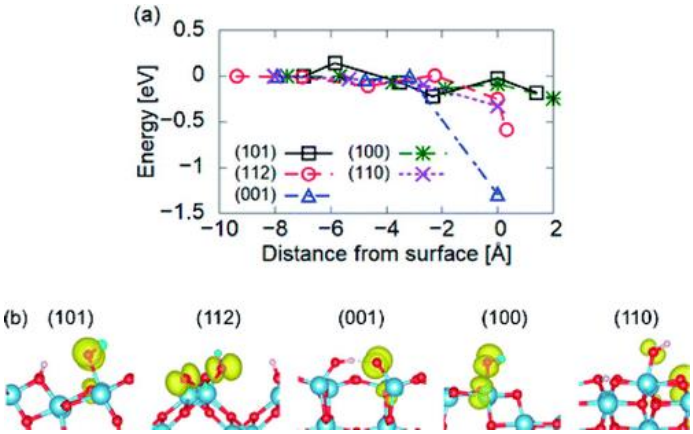

Figure 3. (a) Hole trapping energy at the hydroxylated anatase surfaces. (b) Spin density of a trapped hole (yellow isosurface).

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