Photo-oxidation of Water On Small TiO_2 Nanoparticles[1]

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Ever since the ability of TiO_2 to split water was discovered in 1972, the use of TiO_2 for solar fuel generation has been intensively studied. The high kinetic barrier for photolytic water splitting on TiO_2 surfaces is caused by oxygen evolution reaction in which water is oxidized to O_2. The first of the four one-electron oxidation steps is likely rate limiting; however, the mechanism of this step is controversial.

We have explored the photoreactivity of small hydrated TiO_2 nanoparticles using unconstrained nonadiabatic molecular dynamics simulations (NAMD). Our methodology is based on Tully surface hopping and time-dependent hybrid density functional theory. The results indicate that ultrafast electron-proton transfer from physisorbed water to the photohole initiates the photo-oxidation on the S_1 potential energy surface. The new mechanism readily explains the observation of mobile hydroxyl radicals in recent experiments. Two key driving forces for the photo-oxidation reaction are identified: Localization of the electron-hole pair and stabilization of the photohole by hydrogen bonding interaction.

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